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SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.–Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Meteorology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. – Publisher.

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COMPLEX COMPOUNDS OF TIN. III

T. Sumarokova and I. Litvyak

We prepared [1, 2] mixed complex compounds of the type of $SnCl_4 \cdot 2A \cdot B$ and $SnCl_4 \cdot 2A \cdot 2B$ in which the molecules of addends present in the inner sphere are different from the molecules of addends attached to the sphere.

In the present paper we report on a physico-chemical investigation of the system $SnCl_4 \cdot 2CH_3COOH$-C_6H_5COOH, which demonstrates the existence of the compound $SnCl_4 \cdot 2CH_3COOH \cdot C_6H_5COOH$.

EXPERIMENTAL

The preparation and purification of the starting substances and the experimental procedure have been described previously [1, 2].

The system $SnCl_4 \cdot 2CH_3COOH$-C_6H_5COOH was studied by the methods of electrical conductivity, viscosity and density at 60, 80 and 100°, as well as by means of thermal analysis. Results of measurements are given in Tables 1, 2 and 4; in Table 3 are presented the values of electrical conductivity corrected for viscosity, and the values of the temperature coefficient of electrical conductivity. Property/composition curves are plotted in the diagram.

TABLE 1

Content of C_6H_5COOH		Viscosity (in poises)			Density (g/cm^3)		
weight %	mole %	60°	80°	100°	60°	80°	100°
0.00	0.00	0.149	0.0738	0.0396	1.7933	1.7601	1.7265
2.03	6.03	0.178	0.0804	0.0404	1.7832	1.7459	1.7079
3.93	11.34	0.214	0.0909	0.0454	1.7681	1.7318	1.6931
5.81	16.09	0.235	0.0904	0.0455	1.7683	1.7250	1.6880
9.83	21.90	—	0.0992	0.0485	1.7529	1.7133	1.6760
11.07	26.34	0.273	0.105	0.0513	1.7818	1.6863	1.6500
12.36	30.48	0.295	0.105	0.0527	1.7028	1.6711	1.6337
21.39	45.84	0.358	0.134	0.0648	1.6401	1.6090	1.5817
24.52	50.34	0.360	0.138	0.0630	—	—	—
28.77	55.69	0.344	0.132	—	1.5811	1.5565	1.5287
30.14	57.31	0.332	0.128	0.0561	1.5666	1.5424	1.5132
32.99	60.56	—	0.116	0.0606	—	—	—
37.96	65.61	0.255	0.106	0.0577	—	—	—
43.60	70.00	0.196	0.0884	0.0487	1.4741	1.4495	1.4274
57.28	80.21	0.163	0.0725	0.0430	—	1.3620	1.3400

The viscosity isotherms at all temperatures pass through a maximum corresponding to 50 mole-%. This course of the isotherms is evidence of the occurrence of interaction in the system and indicates the existence of a 1 : 1 compound.

The isotherms of specific electrical conductivity are S-shaped curves. After introduction of a correction for viscosity they are converted into curves with a flat maximum. S-shaped isotherms of electrical conductivity and the occurrence of a maximum on the corrected curve of electrical conductivity

TABLE 2

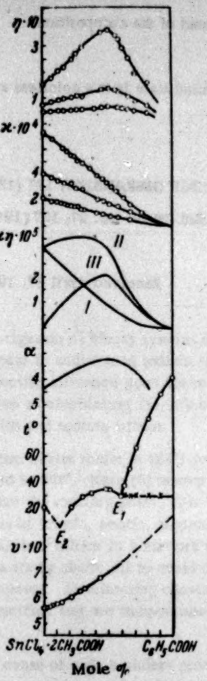
60°		80°		100°	
Content of C_6H_5COOH (mole %)	$\kappa \cdot 10^4$ ($ohm^{-1} \cdot cm^{-1}$)	Content of C_6H_5COOH (mole %)	$\kappa \cdot 10^4$ ($ohm^{-1} \cdot cm^{-1}$)	Content of C_6H_5COOH (mole %)	$\kappa \cdot 10^4$ ($ohm^{-1} \cdot cm^{-1}$)
0.00	2.11	0.00	4.02	0.00	7.30
6.38	1.96	6.03	3.79	6.40	6.77
11.09	1.76	11.34	3.46	14.77	6.04
14.02	1.71	16.09	3.36	19.10	5.73
16.09	1.63	21.90	3.33	21.90	5.61
18.47	1.59	25.90	2.92	23.42	5.45
21.90	1.59	26.34	3.01	26.34	5.15
25.35	1.35	30.48	2.82	30.48	4.83
26.34	1.38	31.75	2.77	36.95	4.50
30.48	1.28	42.20	2.13	41.25	3.97
31.75	1.20	47.30	1.90	45.10	3.65
40.55	0.991	51.03	1.73	48.60	3.35
46.63	0.876	58.84	1.46	52.33	3.07
52.56	0.751	67.00	1.17	55.61	2.76
58.84	0.655			61.81	2.22
67.00	0.512			68.07	1.56
				74.52	1.06
				80.11	0.892

TABLE 3

Content of C_6H_5COOH (mole %)	$\kappa\eta \cdot 10^6$ ($ohm^{-1} \cdot cm^{-1}$)			α (in %)		
	60°	80°	100°	60—80°	80—100°	60—100°
0	31.4	29.6	27.3	4.52	4.07	6.14
10	34.3	30.0	27.2	4.94	4.07	6.52
20	34.8	30.0	27.2	5.19	4.09	6.77
30	35.0	29.5	25.8	5.53	4.09	7.08
40	34.6	27.9	24.5	5.71	4.09	7.12
50	30.0	24.5	20.8	5.79	4.12	7.34
60	19.6	16.9	13.8	5.72	4.03	7.05
70	8.97	8.13	6.93	5.46	3.94	6.56
80	4.86	4.10	2.95	4.60	2.01	6.10

TABLE 4

Content of C_6H_5COOH (mole %)	Temperature of commencement of crystallization	Temperature of crystallization of the eutectic
0.00	19.5°	—
21.96	22.0	—
31.05	29.5	—
37.34	32.5	—
48.73	35.0	—
50.85	35.0	—
61.60	38.0	31.0°
65.96	51.0	29.0
71.04	66.0	30.0
81.58	90.0	30.0
90.98	109.0	30.0
100.00	122.0	



Viscosity, specific electrical conductivity, corrected electrical conductivity, temperature coefficient of electrical conductivity, specific volume and fusibility of the system $SnCl_4 \cdot 2CH_3COOH-C_6H_5COOH$.

are of great interest since the opposite cases have been reported in the literature – disappearance of the maximum of the specific electrical conductivity when the correction for viscosity has been introduced. The electrical conductivity of the system $SnCl_4 \cdot 2CH_3COOH-C_6H_5COOH$ is the resultant of the electrical conductivity due to the acid-base interaction of the components and the actual conductivity of the complex $SnCl_4 \cdot 2CH_3COOH$. We attempted to segregate that portion of the electrical conductivity due to the acid-base interaction. For this purpose we deducted the values of the corrected electrical conductivity of the system $SnCl_4 \cdot 2CH_3COOH-CCl_3COOH$ [2], in which (in our opinion) acid-base interaction does not occur, from the values of the corrected electrical conductivty of the system $SnCl_4 \cdot 2CH_3COOH-C_6H_5COOH$. In such a calculation we make the simplifying assumption that the true electrical conductivity of the complex acid in our system changes with the concentration, as well as when it is diluted with CCl_3COOH. In the diagram, curve II represents the dependence of the corrected electrical conductivity of the system $SnCl_4 \cdot 2CH_3COOH-CCl_3COOH$, and curve I represents that of the system $SnCl_4 \cdot 2CH_3COOH-C_6H_5COOH$. On deducting the values of the corrected electrical conductivity of the system

$$SnCl_4 \cdot 2CH_3COOH-C_6H_5COOH$$

from the values of the corrected electrical conductivity of the system $SnCl_4 \cdot 2CH_3COOH-CCl_3COOH$, we obtained results from which curve III was plotted. As we see from the diagram, this curve passes through a maximum corresponding to equimolar composition and reflects the formation of the compound

$$SnCl_4 \cdot 2CH_3COOH \cdot C_6H_5COOH.$$

Formation of an equimolar compound is also indicated by the temperature coefficient of specific electrical conductivity whose maximum corresponds to 50 mole-%.

The fusion diagram contains two eutectics between which is a distectic point corresponding to 50 mole-%, i.e. to a compound of the composition $SnCl_4 \cdot 2CH_3COOH \cdot C_6H_5COOH$. This compound forms colorless crystals with m.p. 35°. The eutectic E_1, containing 60 mole-% C_6H_5COOH, melts at 30°. The eutectic E_2 and the curve of crystallization of the complex acid $SnCl_4 \cdot 2CH_3COOH$ are shown arbitrarily on the diagram, since we were unable to plot this portion of the diagram due to the high viscosity of the complex acid and of mixtures rich in it.

The isotherms of specific volume point to a contraction which reflects interaction of the components.

Consequently, the data of physico-chemical investigation of the system $SnCl_4 \cdot 2CH_3COOH-C_6H_5COOH$ consistently point to formation of the mixed complex compound $SnCl_4 \cdot 2CH_3COOH \cdot C_6H_5COOH$.

SUMMARY

1. The specific electrical conductivity, the viscosity and the density at 60, 80 and 100°, as well as the fusibility of the system

$$SnCl_4 \cdot 2CH_3COOH-C_6H_5COOH$$

were studied.

2. The results lead to the conclusion that a mixed complex compound of the composition

$$SnCl_4 \cdot 2CH_3COOH \cdot C_6H_5COOH$$

is formed. This compound forms colorless crystals with m.p. 35°; in the fused state it is a colorless and very viscous liquid.

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[2] T. N. Sumarokova and L. I. Maksai, Bull. Sect. Platinum Acad. Sci. USSR, No. 27, 137 (1952).

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THE REACTION OF SODIUM SALTS OF FATTY ACIDS WITH SODIUM NITRITE IN MELTS

N. M. Sokolov

Investigation of binary systems of sodium salts of fatty acids [1] and of systems containing sodium nitrite or thiocyanate in addition to sodium salt of fatty acid [2] has shown that the radical of the salt of the fatty acid exerts a specific influence upon the reactions taking place in the melts. The present work was undertaken with the objective of elucidating the influence of the radical upon the processes taking place between sodium salts of fatty acids and sodium nitrite.

Sodium nitrite melts at 284°; according to Ray [3], Oswald [4] and Oza and Walawalker [5], it decomposes when heated to 320°. Kerp [6] reports the explosion of a mixture of sodium acetate and sodium nitrite when heated above the melting point. Our experiments showed that sodium nitrite is miscible in melts with the sodium salts of formic, acetic, propionic, butyric, isobutyric and isovaleric acids, and these melts withstand reheating. Sodium nitrite in a mixture with the other salts stands up to heating better than when heated alone, but it is necessary above all to avoid overheating, i. e., heating above the temperature at which the given mixture decomposes. Overheating causes the melt to give off a gas, and if heating is then continued, gas formation is intensified and the temperature of the mixture rises spontaneously. Finally, intense flashing and explosion take place.

The cause of such a violent process must be sought in the interaction of the gaseous products of decomposition of sodium nitrite (oxides of nitrogen) with the salt of the fatty acid at high temperature. It must be assumed that the nitrite in itself is not an oxidant in melts of fatty acid salts. Consequently the avoidance of explosion requires that the heating of the melt be stopped as soon as much gas begins to come off.

EXPERIMENTAL

The whole of the work was carried out by the method of visual-polythermal analysis. The salts were melted in a test tube surrounded by a wider test tube to ensure more uniform heating. A glass thread (serving as a stirrer) and a nichrome-constantan thermocouple (in a glass sheath) were also inserted in the test tube. The other junction of the thermocouple was in a Dewar vessel containing ice. The reference curve was plotted from the melting points of water, benzoic acid (122°), manitol (166°), silver nitrate (208°), metallic cadmium (321°), potassium nitrate (337°) and potassium bichromate (398°).

We took chemically pure, commercial preparations of sodium formate, acetate and nitrite and recrystallized them from water. We prepared the remaining salts by the previously described procedure [1] from sodium bicarbonate and the corresponding fatty acid. We used chemically pure sodium bicarbonate but the commercial fatty acids were purified by distillation. The synthesized salts were purified by recrystallization from butyl alcohol. It was impossible to recrystallize them from their aqueous solutions because the concentrated solutions of these salts solidify on cooling. The same effect also occurs on cooling hot solutions in alcohol of some of these salts. It should be mentioned that recrystallization of these salts does not appreciably raise their melting points.

As we see from the liquidus curves (Figs. 1 and 2) there is no complex formation in systems formed by the formate, acetate, isobutyrate and isovalerate. The system formed by the valerate was studied from the nitrite side only to a content of 55% sodium valerate since further increase in valerate content causes decomposition

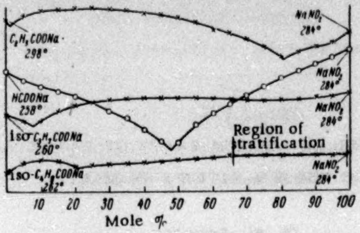

Fig. 1. Liquidus curves of the binary systems.

of the mixture, and the salts also break down when nitrite is introduced into the melt. The liquidus curve has a characteristic form on the portion investigated: the temperature of commencement of crystallization at first rises sharply at the start when a small addition of valerate is made to the nitrite; thereafter, it hardly changes over a considerable part of the diagram (from 5 to 55% valerate). In systems formed by the propionate and butyrate, compounds are formed whose probable compositions are $3C_2H_5COONa \cdot NaNO_2$ and $3C_3H_7COONa \cdot NaNO_2$. In the system isovalerate-nitrite in the region from 66 to 98.4% $NaNO_2$, stratification is observed. The liquidus curve of the system caproate-nitrite could not be prepared since only 0.16% caproate dissolves in fused $NaNO_2$, and the mixture breaks down when nitrite is added to the fused caproate.

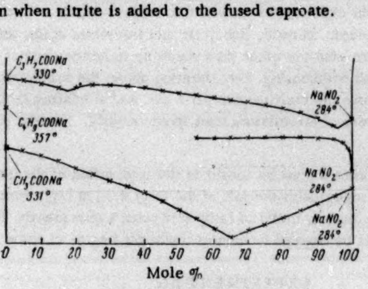

Fig. 2. Liquidus curves of the binary systems

The results obtained are detailed in Tables 1 and 2.

EVALUATION OF RESULTS

Examination of salts of fatty acids in the order of increasing molecular weight shows that the lower members of the series (formate and acetate) do not form compounds with sodium nitrite. Higher members (propionate and butyrate) are capable of forming complexes; this ability disappears in the next member (valerate), and finally (caproate) the ability to mix with nitrite is lost.

We had previously observed a similar picture in the examination of systems containing nitrate and thiocyanate [2]. A comparison of the nitrate systems with the nitrite systems indicates that nitrite forms complexes with salts of fatty acids with the smallest number of carbon atoms in the radical, but this ability disappears when the number of carbon atoms increases, as does also the ability to mix with nitrite in the fused state. Thus, propionate forms a compound with nitrite but not with nitrate, while caproate is substantially immiscible with nitrite but mixes with nitrate.

In systems formed by salts whose radical contains a branched chain, no complexes are formed (systems with isobutyrate and isovalerate). A similar observation was made in systems with sodium thiocyanate and nitrate.

TABLE 1

Binary Systems Formed by Sodium Salts of Fatty Acids and Sodium Nitrite

Sodium nitrite content of mixture (mole %)	Temperature of start of crystallization in systems with						
	formate	acetate	propionate	butyrate	isobutyrate	valerate	isovalerate
0	258°	331°	298°	330°	260°	357°	262°
5	251	327	306	328	253		273
10	243	322	311	325	253		278
15	238	315	312	320	265		276
20	232	306	314	320	271		270
25	225	299	315	324	275		272
30	215	292	313	323	277		273
35	207	285	311	322	279		273
40	193	279	308	320	279		274
45	179	269	306	316	279	323	275
50	177	259	303	314	278	323	277
55	198	248	296	312	278	323	278
60	211	237	286	309	278	323	279
65	222	228	284	306	277	323	282
70	231	237	276	304	276	323	—
75	241	243	269	300	275	323	—
80	251	249	256	296	276	323	—
85	260	258	262	291	277	323	—
90	267	266	267	285	279	321	—
95	275	275	272	276	280	319	—
100	284	284	284	284	284	284	—

TABLE 2

Intersection of Liquidus Curves in Systems Formed by Sodium Salts of Fatty Acids and Sodium Nitrite

Systems	Position of coordinate of eutectic point on liquidus curves	
	temperature	sodium nitrite content (mole-%)
Formate-nitrite	169°	48
Acetate-nitrite	227	65
Propionate-nitrite	293 254	1.4 80.5
Butyrate-nitrite	317 274	17.5 96
Isobutyrate-nitrite	247	8
Valerate-nitrite	282	0.04
Isovalerate-nitrite	269	21

The investigation of the present systems largely confirmed our earlier conclusions about the influence of structure and size of salt radical, on the processes in melts which we reached on the basis of study of 16 binary systems containing thiocyanate and nitrate and 28 binary systems containing only sodium salts of fatty acids.

I take the opportunity of expressing thanks to A. G. Bergman for his valuable guidance.

SUMMARY

1. Eight binary systems formed by salts of fatty acids with sodium nitrite were investigated by the visual-polythermal method of physico-chemical analysis.

2. It was shown how the properties of salts of fatty acids in the melt change with changing number of atoms in the radical and with the isomeric form.

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DECOMPOSITION OF ETHYL NITRATE UNDER THE ACTION OF STRONG ACIDS

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Some of the investigators of the nitration of organic compounds with nitric acid have attempted to replace the acid by its esters, in particular by ethyl nitrate. It was found that ethyl nitrate alone does not react with organic compounds [1], although Boedtker [2] found that benzene can be nitrated in presence of $AlCl_3$. A closer study of the nitration of benzene with ethyl nitrate in presence of various substances was undertaken by B. V. Tronov [3-5]. He found that the only substances to exert a catalytic action were $AlCl_3$, $SnCl_4$, $SbCl_5$ and $FeCl_3$. This author suggested that the chlorides in question form complex compounds with ethyl nitrate, which also function as the nitrating agents during reaction with benzene. $AlCl_3$, $SnCl_4$ and $SbCl_5$ decompose ethyl nitrate explosively. This fact complicates and hinders the isolation and study of the complex compounds of ethyl nitrate with the chlorides.

It is known, on the other hand, that ethyl nitrate nitrates aromatic compounds in presence of sulfuric acid [6-10]. Raudnitz [9], for example, developed a method of nitration of aromatic compounds with a mixture of ethyl nitrate and sulfuric acid at low temperature. He showed that anthraquinone is nitrated to dinitroanthraquinone while phenol is converted into 2, 4, 6-trinitrophenol. The American investigator Kuhn [11] associates the nitrating action of ethyl nitrate in sulfuric acid with formation of the nitronium ion NO_2^+ due to ionization of ethyl nitrate in sulfuric acid. Dissociation of ethyl nitrate in sulfuric acid was confirmed by the cryoscopic and spectroscopic studies of Hantzsch [12] and Kuhn [11]. According to the latter author it proceeds according to the scheme:

$$RONO_2 + H_2SO_4 = RONO_2H^+ + HSO_4^-,$$
$$RONO_2H^+ = ROH + NO_2^+,$$
$$ROH + 2H_2SO_4 = ROSO_3H + H_3O^+ + HSO_4^-.$$

Our preliminary experiments showed that at higher temperature (20° and above) sulfuric acid causes rapid decomposition of ethyl nitrate with evolution of oxides of nitrogen. This reaction is analogous with the breakdown of ethyl nitrate under the action of $AlCl_3$, $SnCl_4$ and $SbCl_5$.

On the basis of the data in the literature, we suggest that the catalytic influence of sulfuric acid and the chlorides of aluminum, tin and antimony on the nitration of organic compounds by ethyl nitrate is associated with the acidic properties of sulfuric acid and the chlorides. H_2SO_4, $AlCl_3$, $SnCl_4$ and $SbCl_5$ are known to be strong acids. Their acid-base reaction with ethyl nitrate evidently leads to formation of unstable complexes. Thus the acid-base interaction of ethyl nitrate and sulfuric acid might be expressed by the scheme:

$$C_2H_5ONO_2 + 2H_2SO_4 \rightleftarrows [C_2H_5ONO_2H_2]^{++} + 2HSO_4^-$$

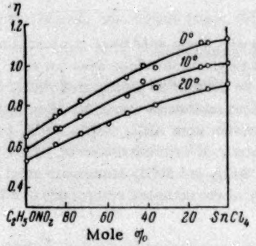
In the nitration of organic compounds with ethyl nitrate in presence of the above catalysts, the nitrating agents are either the unstable complex compounds alone (as suggested by B. V. Tronov) or the oxides of nitrogen resulting from the breakdown of the complexes. To test this conclusion, we decided to investigate the formation of intermediate compounds of ethyl nitrate with tin chloride by the methods of physico-chemical analysis, and also to study the thermal conditions and the products of decomposition of ethyl nitrate under the action of strong acids (H_2SO_4, $SnCl_4$ and HNO_3).

EXPERIMENTAL

1. Viscosity, Density and Electrical Conductivity of the System $SnCl_4$-$C_2H_5ONO_2$

We studied the system tin chloride-ethyl nitrate by measuring the viscosity, density and electrical conductivity at 0, 10 and 20°, i. e., at temperatures at which decomposition of ethyl nitrate in presence of $SnCl_4$ is not observed. The density was measured with a pycnometer and the relative viscosity by observation of the rate of efflux. The reactants were purified by distillation and were stored in sealed ampoules. Ethyl nitrate had b.p. 84-84.5° at 695 mm and d_{20}^{20} 1.108. Tin chloride was used with b.p. 110.5° at 700 mm.

Our measurements showed that the system does not conduct the electric current. The viscosity isotherms (see diagram and table) are concave to the axis of composition; the isotherms of the logarithm of the viscosity also show a positive deviation from rectilinearity which points to interaction of the components. The isotherms of specific volume are rectilinear. Consequently, on the basis of the character of the dependence of viscosity and logarithm of viscosity on composition, expressed as molar percentages, we may conclude that ethyl nitrate forms a complex compound with tin chloride. The form of the viscosity isotherm provides no information about the composition of the compound.



Dependence of viscosity on composition.

2. Decomposition of Ethyl Nitrate in Presence of Tin Chloride

The decomposition of ethyl nitrate in presence of tin chloride was studied at various temperatures. We followed the reaction by the change of temperature inside the reaction mixture. A mixture containing 0.05 mole $SnCl_4$ and 0.1 mole ethyl nitrate was prepared. At 20° the mixture is homogeneous and light-yellow. The color disappears at lower temperatures and changes to dark-yellow at higher temperatures. Fine yellow crystals gradually started to deposit on the walls of the flask containing the reaction mixture. After a short period of time (depending on the temperature of the mixture), self-accelerating breakdown of the crystals commenced, followed by decomposition of the liquid with evolution of NO and NO_2. At the same time the temperature of the reaction mixture rose rapidly and reached 120-130° after one minute; it then fell rapidly since the reaction ceased. The period of time between the moment of adding the tin chloride to ethyl nitrate and the start of reaction depends in great measure on the temperature of the surrounding medium. Thus, at 25° the reaction starts 3 hours after addition of $SnCl_4$ to ethyl nitrate, while at 50° it starts after 15 minutes. At 23-40° nitric oxide was evolved during decomposition of ethyl nitrate; at higher temperatures both nitric oxide and nitrogen dioxide were observed. The gaseous products of reaction were not subjected to more detailed examination. From the mixture of liquid reaction products (a viscous, dark-yellow, transparent mass with an ethereal odor) we succeeded by fractional distillation in isolating a minute quantity of ethyl acetate and acetic acid. By qualitative reactions we detected traces of acetaldehyde. A part of the ethyl nitrate did not react. Experiments on the nitration of benzene with ethyl nitrate in presence of $SnCl_4$ at 80° showed that about 36% of nitrobenzene is formed (calculated on the ethyl nitrate) if the starting substances are taken in the following proportions: 0.05 mole $SnCl_4$, 0.1 mole ethyl nitrate and 0.2 mole benzene. This result is in good agreement with the results of B. V. Tronov [5].

3. Decomposition of Ethyl Nitrate Under the Action of Sulfuric Acid

Experiments showed that decomposition of ethyl nitrate by sulfuric acid (d 1.84) commences at 23-24°, continues with self-acceleration and heat development, and becomes instantaneous at 30°. After one minute the temperature of the mixture reaches 85°. After 3-4 minutes the temperature of the reaction mixture starts to fall and the reaction slowly ceases. The reaction comes to an end 40-42 minutes after the start of the experiment, and the temperature of the reaction mixture commences to fall more rapidly. This change of temperature of the reaction mixture (reflecting the thermal effect of the reaction) is observed when using 0.1 mole H_2SO_4 to 0.2 mole ethyl nitrate. If the proportion of sulfuric acid is doubled, the reaction goes more slowly and comes to an end only 55-56 minutes after the start of the experiment. Part of the ethyl nitrate remains unreacted. Oxides of nitrogen (NO and NO_2) and carbon dioxide are evolved during the reaction. Liquid products isolated were formic acid and a very small quantity of an ester that we assume to be ethyl formate.

Viscosity and Density of the System Ethyl Nitrate-Tin Chloride

Ethyl nitrate (mole %)	Ethyl nitrate (weight-%)	Temperature	Density	Relative viscosity
100	100	0°	1.136	0.65
		10	1.121	0.58
		20	1.108	0.53
84.9	66	0	1.373	0.75
		10	1.359	0.69
		20	1.345	0.61
82.9	60.7	0	1.417	0.77
		10	1.402	0.69
		20	—	—
72.9	48.5	0	1.536	0.82
		10	1.523	0.75
		20	1.503	0.66
49.9	25.8	0	1.814	0.94
		10	1.796	0.85
		20	1.776	0.76
42.3	20.4	0	1.876	1.00
		10	1.880	0.92
		20	—	—
36.3	16.6	0	1.956	0.99
		10	1.939	0.89
		20	1.922	0.80
13.5	5.2	0	1.737	1.11
		10	1.711	0.99
		20	—	—
10.4	3.9	0	2.194	1.11
		10	2.174	1.00
		20	2.148	0.88
0	0	0	2.281	1.13
		10	2.258	1.01
		20	2.226	0.91

We also studied the nitration of benzene with ethyl nitrate in presence of sulfuric acid. Nitration was conducted at 78° (temperature in the interior of the reaction mixture) with vigorous stirring. Using 0.05 mole sulfuric acid, 0.1 mole ethyl nitrate and 0.2 mole benzene, nitration to nitrobenzene after 4 hours was 12% or the equivalent of 23% of the amount of ethyl nitrate taken.

4. Decomposition of Ethyl Nitrate Under the Action of Nitric Acid

In a study of the system ethyl nitrate-nitric acid, on the basis of viscosity, density and electrical conductivity at 0, 10 and 20°, M. I. Usanovich and T. Sushkevich [13] showed that nitric acid is inert to ethyl nitrate. Nitration of organic compounds with a mixture of nitric acid and ethyl nitrate goes at the expense of the nitric acid, and the yield of nitro products is proportional to the concentration of HNO_3. We established, however, that at temperatures above 40°, nitric acid (d 1.52) causes partial decomposition of ethyl nitrate. This reaction was found to be accompanied by slight rise of temperature (by 20-25°) and by stratification; part of the ethyl nitrate remains unreacted (composition of reaction mixture: 0.1 mole HNO_3 to 0.1 mole ethyl nitrate). Oxides of nitrogen (NO and NO_2) and carbon dioxide are given off during the reaction.

If the oxides of nitrogen are previously broken down in the nitric acid by boiling with urea nitrate, the ethyl nitrate is not decomposed even at its boiling point (86°). This behavior indicates that ethyl nitrate breaks down slowly in nitric acid due to the presence of oxides of nitrogen, but molecules of HNO_3 itself do not participate in the reaction.

SUMMARY

1. The system tin chloride-ethyl nitrate was studied on the basis of measurements of viscosity, density and electrical conductivity. The form of the viscosity isotherms indicates interaction in the system.

2. The thermal effect and the products of decomposition of ethyl nitrate in presence of H_2SO_4, $SnCl_4$ and HNO_3 were studied. Decomposition of ethyl nitrate is a self-accelerating process and proceeds with release of oxides of nitrogen. Sulfuric acid causes ethyl nitrate to break down to formic acid and carbon dioxide, while tin chloride leads to formation of acetic acid. In nitric acid, ethyl nitrate is oxidized by oxides of nitrogen with formation of carbon dioxide.

3. It is suggested that the decomposition of ethyl nitrate under the action of strong acids (H_2SO_4, $SnCl_4$, $SbCl_5$ and $AlCl_3$) precedes the formation of unstable complex compounds due to acid-base interaction of ethyl nitrate with these acids.

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DIELECTRIC PROPERTIES OF THE SYSTEMS ACETIC ACID - PYRIDINE (ANILINE) IN BENZENE

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Physico-chemical analysis of systems consisting of acetic acid and pyridine or aniline is of definite interest for the purpose of elucidation of the composition of the compounds formed, since the products of interaction of the components cannot be individualized. There is evidence that acetic acid is associated to dimer and polymer in the liquid state. Dimeric molecules of acetic acid, formed by hydrogen bonds with an energy of 14-16 kcal/ mole [1], are fairly stable: they can be kept in solutions of nonpolar solvents such as benzene, and do not break down even when the acid passes into the vapor state.

During formation of compounds with amines, acetic acid can enter into reaction in the form of polymers, dimers or monomer.

Systems formed from acetic acid with pyridine or aniline were subjected to numerous physico-chemical investigations of various properties. In the system acetic acid-aniline, the composition of the resultant compound was established with great certainty. On the other hand, in the system acetic acid-pyridine very conflicting results were obtained, probably due to the weak interaction of the components and to the inadequate sensitivity of the methods employed.

In the present investigation we had in mind the application of our proposed method of study of the dielectric properties of solutions to complex systems in which chemical reaction proceeds side by side with breakdown of the associated substances. We also wished to take advantage of the high sensitivity of this method for obtaining more exact knowledge of the composition of the compounds formed in the systems acetic acid-aniline and acetic acid-pyridine. The investigation was carried out in benzene (a solvent indifferent to the reactants).

The viscosity and specific volumes of the solutions were studied, in addition to the dielectric properties.

The method of physico-chemical analysis of solutions, based on study of the deviations of the dielectric constant or dielectric polarization from additivity, has been explained in earlier publications [2]. The method depends upon the formation of a new donor-acceptor coordinative bond when complexes or molecular compounds are formed between molecules of the reactants; this new bond causes the electronic density between the bonded atoms to change. The change is reflected in the magnitude of the total polarization of the molecules and is manifested in the magnitude of the dipole moment and of the total dielectric polarization of the reactants. Due to this, the dielectric constant of the solution is increased.

The total polarization of interacting substances in a ternary system (A-B-solvent) is calculated from an equation based on the miscibility law:

$$P_{2,3}=\frac{1000}{n}\left[f(\varepsilon)-kd\right]+k\left[aM_1+bM_2\right], \tag{1}$$

where n and ϵ are the molality and dielectric constant of the solution, M_1 and M_2 are the molecular weights of the reactants, a and b are their molar proportions in the solution, k is a constant for the solvent; $k = f(\epsilon_0)\cdot\frac{1}{d_0}$, where ϵ_0 and d_0 are the dielectric constant and the specific gravity of the solvent. As the value of $f(\epsilon)$ we may take the specific polarization as expressed by Clausius and Mosotti $[f(\epsilon) = \frac{\epsilon - 1}{\epsilon + 2}]$ or as expressed by Onsager and Kirkwood $[f(\epsilon) = \frac{(\epsilon - 1)(2\epsilon + 1)}{9\epsilon}]$.

The position of the maximum of the deviations of the dielectric polarization on the composition property diagram, which indicates the composition of the compounds formed in the solution, does not depend upon the form of $f(\epsilon)$. With low concentrations and low values of ϵ, the magnitudes of the polarization and their deviations ΔP are similar among themselves and do not depend upon the representation of the specific polarization. For solutions with a high concentration and a large dielectric constant, the use of $f(\epsilon)$ with the Clausius-Mosotti relation leads to too-low values of the polarization since this expression does not take account of the internal field of the neighbouring molecules.

The dielectric theory of Onsager and Kirkwood more fully reflects the reciprocal influence of the polar molecules in the individual liquids and solutions; the molar polarization in concentrated solutions is therefore preferably determined with the help of an equation in which the Onsager-Kirkwood specific polarization is used to represent $f(\epsilon)$. Equation (1) can then be rearranged to:

$$P_{2,3} = \frac{1000}{n}\left[\frac{(\varepsilon - 1)(2\varepsilon + 1)}{9\varepsilon} - kd\right] + k\,[aM_1 + bM_2], \tag{2}$$

$$k = \frac{(\varepsilon_0 - 1)(2\varepsilon_0 + 1)}{9\varepsilon_0} \cdot \frac{1}{d_0}$$

The increment of molar polarization ΔP, being due to complex formation, is calculated from the formula

$$\Delta P = \frac{1000 \cdot \Delta\varepsilon}{9n}\left|2 + \frac{1}{\varepsilon_{\text{exp.}} \cdot \varepsilon_{\text{calc}}}\right| - \frac{1000k \cdot \Delta v}{n \cdot v_{\text{exp.}} \cdot v_{\text{calc.}}}, \tag{3}$$

where $\epsilon_{\text{exp.}}$, $\epsilon_{\text{calcd.}}$, $v_{\text{exp.}}$, $v_{\text{calcd.}}$, are the experimental and calculated values of the polarization and specific volumes: $\Delta\epsilon = \epsilon_{\text{exp.}} - \epsilon_{\text{calcd.}}$, $\Delta v = v_{\text{calcd.}} - v_{\text{exp.}}$

Solutions used in the measurements were prepared by the method of isomolar concentrations: the total molar concentration of the mixture was kept constant and the ratio of the reactants was altered. The dielectric constants were determined for 4, 2, 1 and 0.1 molar solutions, and the specific volumes for 4 and 2 molar concentrations. The principal measurements were performed at a temperature of 20.00 ± 0.02° which was maintained with the help of an ultrathermostat. The dielectric constants were determined by the beat method (wavelength 301.3 m).

System Acetic Acid-Aniline in Benzene

The binary system has been repeatedly studied. Measurements have thus been made of the electrical conductivity of the system acetic acid-aniline [3-12] and of its temperature coefficient [11], of the viscosity [4, 9, 12-15, 20] and the temperature coefficient of viscosity [12], of the density [4, 8, 10, 12-17, 20], of the refractive index [14, 17-21], of the magnetic rotation of the plane of polarization [6], of the fusion diagram [22, 23] and of the ionic transfer [24a]. Chemical interaction in the system was reported in these studies, but only in some of them were any conclusions drawn about the composition of the compounds formed. Reference was made to possible formation of the compounds $C_6H_5NH_2 \cdot 2CH_3COOH$, $C_6H_5NH_2 \cdot CH_3COOH$ and $2C_6H_5NH_2 \cdot \cdot CH_3COOH$. The existence of the first of these was convincingly demonstrated by a study of the fusion, viscosity, electrical conductivity and its temperature dependence, and the deviations of the refractive indices. Its existence was quite clearly reflected on the diagrams of the properties mentioned. Formation of the second and third compound is hypothetical; there are merely indications that the compounds are metastable [23].

Results of investigations of the dielectric properties of the system acetic acid-aniline in benzene at various concentrations are presented in Table 1 and Fig. 1. Data for viscosity and specific volumes and their deviations from additivity are presented in Table 2 and Fig. 2. The viscosity was determined in hermetically closed viscosimeters of the Ostwald type.

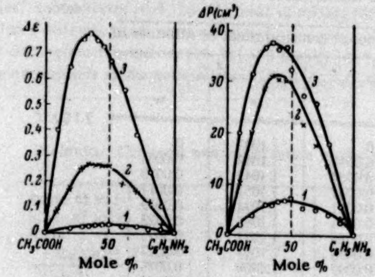


Fig. 1. Dielectric properties of the system acetic acid-aniline in benzene.
Concentration of solutions: 1) 1 M; 2) 2 M; 3) 4 M.

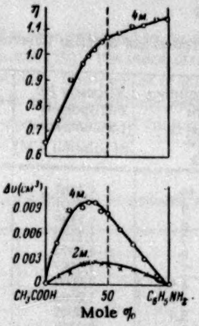


Fig. 2. Specific volumes and viscosity of the system acetic acid-aniline in benzene.

TABLE 1

Dielectric Constants and Polarization of the System Acetic Acid-Aniline in Benzene at 20°

Ratio of volumes of solutions $\frac{V_{CH_3COOH}}{V_{C_6H_5NH_2}}$	n = 4 M.			n = 2 M.			n = 1 M.		
	ϵ exp.	$\Delta\epsilon$	ΔP (cm^3)	ϵ exp.	$\Delta\epsilon$	ΔP (cm^3)	ϵ exp.	$\Delta\epsilon$	ΔP (cm^3)
0 : 10	3.817	0	0	3.006	0	0	2.626	0	0
1 : 9	3.798	0.107	6.0	2.980	0.031	3.4	2.613	0.013	3.0
2 : 8	3.804	0.239	17.9	3.016	0.123	14.3	2.590	0.017	3.9
3 : 7	3.822	0.384	25.9	2.990	0.154	17.9	2.569	0.022	5.1
4 : 6	3.875	0.562	27.4	2.967	0.187	21.8	2.544	0.023	5.2
5 : 5	3.858	0.671	32.5	2.982	0.259	30.2	2.526	0.031	7.4
5.5 : 4.5	3.854	0.730	35.9	2.955	0.260	30.4	2.511	0.030	7.0
6 : 4	3.811	0.750	36.4	2.927	0.261	30.5	2.496	0.028	6.5
6.5 : 3.5	3.772	0.774	37.7	2.905	0.267	31.3	2.481	0.026	6.0
7 : 3	3.683	0.748	36.9	2.856	0.247	28.9	2.467	0.025	6.0
8 : 2	3.459	0.651	31.7	2.725	0.172	20.2	2.433	0.017	4.0
9 : 1	3.083	0.401	20.0	2.585	0.089	10.5	2.397	0.008	1.9
10 : 0	2.556	0	0	2.440	0	0	2.363	0	0

Calculations of the viscosity were based on the assumption that water at 20° has a value of 0.010046 poise [24].

The following conclusions can be drawn from the results. The position of the maximum of deviation of the dielectric constant and polarization, as also the values of specific volumes and internal friction, show that in concentrated solutions (4 M) of acetic acid in benzene, the compound $C_6H_5NH_2 \cdot 2CH_3COOH$ is formed, i. e. of the same composition as in the absence of solvent. With decreasing concentration of the reactants in solution, the maxima of deviations on the ΔP composition and Δε composition diagrams are shifted, and at 1 M concentration the maximum already corresponds to 1 : 1 ratio. This testifies to the formation in the system of compounds whose composition depends upon the concentration of the solutions. Up to the present time, the compound $C_6H_5NH_2 \cdot CH_3COOH$ has not been reported in the literature. Apparently it is only formed in solutions.

TABLE 2

Internal Friction and Specific Volumes of the System Acetic Acid-Aniline in Benzene at 20°

Ratio of volumes of solutions $\frac{V_{CH_3COOH}}{V_{C_6H_5NH_2}}$	Viscosity (in centipoises) (concentration of solution 4 M)	Specific volumes at concentrations of solutions of			
		4 M.		2 M.	
		v	Δv	v	Δv
0 : 10	1.1467	1.0710	0	1.1031	0
1 : 9	1.1391	1.0727	0.0010	1.1042	0.0004
2 : 8	1.1136	1.0735	0.0030	1.1049	0.0013
3 : 7	1.1109	1.0745	0.0047	1.1061	0.0017
4 : 6	1.0872	1.0753	0.0067	1.1074	0.0019
5 : 5	1.0687	1.0764	0.0084	1.1086	0.0023
5.5 : 4.5	1.0500	1.0771	0.0086	1.1092	0.0025
6 : 4	1.0284	1.0780	0.0095	1.1098	0.0027
6.5 : 3.5	1.0045	1.0792	0.0097	1.1108	0.0025
7 : 3	0.9750	1.0813	0.0090	1.1117	0.0024
8 : 2	0.9013	1.0843	0.0087	1.1143	0.0013
9 : 1	0.7437	1.0908	0.0050	1.1165	0.0007
10 : 0	0.6629	1.0986	0	1.1188	0

Mention was made above of a compound $2C_6H_5NH_2 \cdot CH_3COOH$. No evidence of the formation of this compound in benzene solution was obtained in our investigations.

System Acetic Acid-Pyridine in Benzene

The system acetic acid-pyridine has been investigated with reference to a whole series of properties, and it can be characterized as a typical irrational system. Interaction of the components in this system is manifested to approximately the same extent as between acetic acid and aniline. This is apparent on comparing the thermal

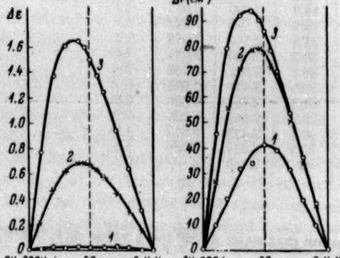


Fig. 3. Dielectric properties of the system acetic acid-pyridine in benzene.
Concentrations of solutions: 1) 0.1 M; 2) 2 M; 3) 4 M.

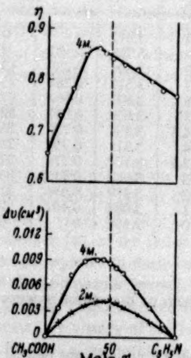


Fig. 4. Specific volumes and viscosity of the system acetic acid-pyridine in benzene.

effects of mixing: for the system $C_6H_5NH_2$-CH_3COOH the thermal effect is 6.9 kcal/mole; for C_5H_5N-CH_3COOH it is 6.5 kcal/mole [25]. However, on the composition/property diagrams the experimental points are more weakly reflected for various physico-chemical measurements in this system and they frequently indicate compounds of various compositions.

The binary system acetic acid-pyridine in the liquid phase has been examined by measurements of electrical conductivity [6-8, 26-28], heat of mixing [25] and vapor pressure [19]. The fusion diagram [22, 28] contains a distectic point corresponding to the compound $C_5H_5N \cdot CH_3COOH$. Investigation of the viscosity [4, 13, 29-32], refractive indices [19-21] and density [4, 7, 13, 20] indicates that the maximum deviation from additivity corresponds to the composition $C_5H_5N \cdot 4CH_3COOH$. There are also indications of the possible formation of

TABLE 3

Dielectric Constants and Polarization of the System Acetic Acid-Pyridine in Benzene at 20°

Ratio of volumes of solutions $^{V}CH_3COOH$ / $^{V}C_3H_5N$	$n = 4$ м.			$n = 2$ м.			$n = 0.1$ м.		
	ϵ exp.	Δε	ΔP (cm³)	ϵ exp.	Δε	ΔP (cm³)	ϵ exp.	Δε	ΔP (cm³)
0 : 10	5.249	0	0	3.630	0	0	2.342	0	0
1 : 9	5.299	0.319	18.0	3.661	0.150	17.3	2.341	0.004	9.7
2 : 8	5.339	0.629	35.6	3.687	0.295	34.1	2.340	0.008	19.4
3 : 7	5.383	0.942	53.4	3.710	0.437	50.5	2.340	0.013	31.5
4 : 6	5.401	1.229	69.8	3.730	0.576	66.7	2.338	0.016	38.8
4.5 : 5.5	5.416	1.379	78.4	3.715	0.621	72.0	—	—	—
5 : 5	5.405	1.503	85.5	3.699	0.664	77.1	2.333	0.017	41.3
5.5 : 4.5	5.359	1.591	90.5	3.655	0.680	79.0	—	—	—
6 : 4	5.277	1.644	93.7	3.590	0.674	78.5	2.327	0.016	33.8
7 : 3	4.977	1.613	92.3	3.407	0.610	71.3	2.319	0.013	31.6
8 : 2	4.468	1.373	79.0	3.148	0.470	55.3	2.309	0.008	19.4
9 : 1	3.596	0.771	44.9	2.781	0.222	26.4	2.300	0.004	9.7
10 : 0	2.556	0	0	2.440	0	0	2.291	0	0

TABLE 4

Internal Friction and Specific Volumes of the System Acetic Acid-Pyridine in Benzene at 20°

Ratio of volumes of solutions $^{V}CH_3COOH$ / $^{V}C_5H_5N$	Viscosity (in centipoises) (concentration of solutions 4 M)	Specific volumes at concentrations of solutions			
		4 м.		2 м.	
		v	Δv	v	Δv
0 : 10	0.7702	1.0941	0	1.1154	0
1 : 9	0.7857	1.0929	0.0016	1.1147	0.0011
2 : 8	0.8005	1.0915	0.0035	1.1140	0.0020
3 : 7	0.8227	1.0901	0.0053	1.1137	0.0027
4 : 6	0.8270	1.0884	0.0075	1.1133	0.0035
4.5 : 5.5	—	1.0879	0.0081	1.1130	0.0039
5 : 5	0.8433	1.0877	0.0086	1.1126	0.0044
5.5 : 4.5	0.8504	1.0875	0.0090	1.1130	0.0042
6 : 4	0.8625	1.0878	0.0089	1.1133	0.0041
7 : 3	0.8520	1.0884	0.0087	1.1140	0.0037
8 : 2	0.7813	1.0904	0.0072	1.1153	0.0028
9 : 1	0.7345	1.0947	0.0033	1.1167	0.0016
10 : 0	0.6629	1.0985	0	1.1187	0

the compounds $3C_5H_5N \cdot 2CH_3COOH$ and $2C_5H_5N \cdot 3CH_3COOH$ [32]. The physico-chemical investigations of the binary system pyridine-acetic acid therefore do not provide clear-cut evidence of the composition of the compounds formed; this is evidently due to the weak manifestation of chemical interaction in the system and to the important part played by van der Waals forces.

We studied this system in benzene, bearing in mind that in an indifferent solvent the van der Waals forces will be considerably weakened and the chemical interaction will be more clearly detectable. We studied the system acetic acid-pyridine in benzene with reference to the internal friction, the specific volume and the dielectric properties. Results are shown in Tables 3 and 4, Figs. 3 and 4.

The data show that in benzene solutions, acetic acid forms compounds with pyridine (just as with aniline) whose composition depends on the concentration of reactants. At 4 M concentration of solutions, the isotherms of the investigated properties most definitely indicate the formation in solution of the compound $C_5H_5N \cdot 2CH_3COOH$. In the region of lower concentrations (1-0.1 M) the predominant product is $C_5H_5N \cdot CH_3COOH$.

The effect of temperature on the position of the maximum of deviations $\Delta\epsilon$ and ΔP was studied for 1 M solutions. The position of the maxima in the temperature range of 20 to 50° does not change (Fig. 5).

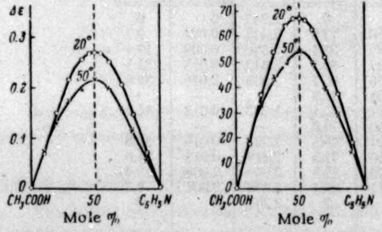
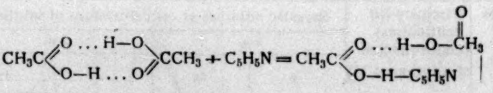


Fig. 5. Effect of temperature on the deviation of the dielectric constant and polarization in the system acetic acid-pyridine in benzene. Concentration of solutions 1 M.

The sharpness of the maxima on the composition/property diagrams and our consistent results in benzene solutions are partly accounted for by the constant degree of association of acetic acid in benzene solutions (dimers) as contrasted with the existence of molecules of various degrees of polymerization in the pure substance.

The bonding energy of molecules of amines with an acid is greater than the energy of the hydrogen bond in the dimeric molecule of acetic acid. This is evidenced by the positive thermal effect of mixing of acetic acid with pyridine and aniline. For this reason, the interaction of amines (aniline and pyridine) with acetic acid in concentrated solutions (4 M) may be represented by a scheme involving rupture of one hydrogen bond in the dimer of acetic acid, for example:



In more dilute solutions the solvent (benzene) causes the complex $C_5H_5N \cdot 2CH_3COOH$ to break down with formation of the compound $C_5H_5N \cdot CH_3COOH$ which is more stable under these conditions and can be detected in dilute solutions.

Mezhetsky [33, 34] has recently studied the Raman spectra of the system pyridine-acetic acid and has established that the strongest interaction is observed in a mixture containing from 30 to 41.4% pyridine, which corresponds to the composition of the compounds that we detected in concentrated benzene solutions.

The agreement between the results obtained by study of Raman spectra and dielectric properties of the system acetic acid-pyridine arises from the fact that both methods are based on one and the same process – the formation of a new chemical bond due to acid-base interaction of acetic acid and pyridine.

Comparison of the magnitudes of ΔP of systems acetic acid-aniline and acetic acid-pyridine shows that at equal concentrations the deviation of the polarization ΔP is always higher for the second system than for the first. It follows therefore that in benzene solutions, just as in aqueous solutions, pyridine is a stronger base than aniline.

We see from the foregoing data that the method of physico-chemical analysis of solutions based on determination of their dielectric properties is an extremely sensitive tool for the detection of processes of intermolecular interaction and is suitable for the study of systems whose components are associated, as well as for the study of acid-base interaction in nonaqueous media.

SUMMARY

1. A study was made of the dielectric properties, viscosity and specific volumes of systems comprising acetic acid and aniline or pyridine in benzene.

2. The maxima of the deviations of the dielectric constants and polarization and of the specific volumes from additivity and the discontinuities on the viscosity diagrams show that molecular compounds are formed by acetic acid with amines whose composition depends on the concentration of the solutions. The compounds $C_6H_5NH_2 \cdot 2CH_3COOH$ and $C_5H_5N \cdot 2CH_3COOH$ exist in concentrated solutions; equimolar compounds $C_6H_5NH_2 \cdot CH_3COOH$ and $C_5H_5N \cdot CH_3COOH$ are present in dilute solutions.

3. On the basis of the magnitude of the maximum deviation of the polarization, it is concluded that in benzene solutions, just as in aqueous solutions, pyridine is a stronger base than aniline.

4. It is shown that the method of physico-chemical analysis of solutions, based on determination of their dielectric properties, is also suitable for the study of systems whose components are associated, and that it can be successfully applied to the study of acid-base interaction in nonaqueous media.

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THE SURFACE TENSION IN THE SYSTEM ANILINE-ACETIC ACID

I. M. Bokhovkin

The existence of the compound $2CH_3COOH \cdot C_6H_5NH_2$ was established [1] from the fusion diagram of the system aniline-acetic acid. Studies of the conductivity, viscosity and density showed that the compound in question also exists in a dilute homogeneous medium. The isotherms of conductivity at −6.8 and 0° have a minimum corresponding to the composition of the compound $2CH_3COOH \cdot C_6H_5NH_2$, while the isotherms of viscosity have a pronounced maximum. Rise of temperature leads to flattening of the minimum of the electrical conductivity and of the maximum of the viscosity, indicating marked dissociation of the compound [2].

It was of interest to investigate the system aniline-acetic acid by the method of measurement of surface tension in order to obtain further evidence of the existence of the compound in a dilute homogeneous medium and to observe its effect on the form of the surface tension isotherms.

The surface tension was investigated by the method based on the maximum pressure of a gas bubble proposed by P. A. Rebinder [3]. The starting substances were purified before the experimental work (the acetic acid by freezing and the aniline by double distillation).

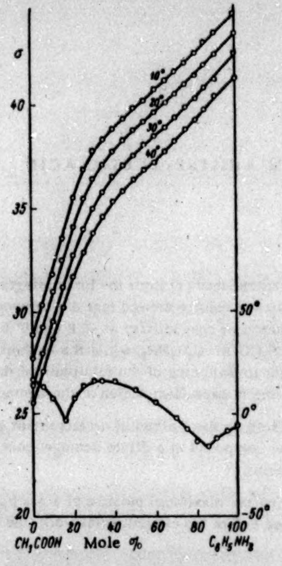
Measurements of surface tension were performed at 10, 20, 30 and 40°. Results were expressed in dynes/ /cm; concentrations were expressed as mole-%.

On the basis of the experimental data (table) isotherms of surface tension were plotted on the same diagram as the fusion curve.

With progressive addition of aniline to acetic acid, the surface tension isotherms at first rise steeply, but after addition of about 30% aniline their slope becomes much more gradual. We associate the presence of a discontinuity on the surface tension isotherms with the existence of a compound in the diluted medium. This discontinuity flattens out slightly with rising temperature and shifts in the direction of the aniline, pointing to dissociation of the compound $2CH_3COOH \cdot C_6H_5NH_2$ with rising temperature.

Surface Tension in the System Acetic Acid-Aniline

$C_6H_5NH_2$ (mole-%)	Surface tension (dynes/cm)				$C_6H_5NH_2$ (mole-%)	Surface tension (dynes/cm)			
	10°	20°	30°	40°		10°	20°	30°	40°
5	30.45	29.31	28.01	27.12	55	40.21	39.22	38.05	36.83
10	32.01	31.02	29.55	28.69	60	40.75	39.68	38.50	37.25
15	33.75	32.55	31.35	30.40	65	41.19	40.12	38.99	37.78
20	35.60	34.15	32.72	31.75	70	41.62	40.54	39.38	38.26
25	36.93	35.50	34.00	32.91	75	42.04	40.99	39.87	38.81
30	37.85	35.51	35.05	33.95	80	42.50	41.41	40.35	39.30
35	38.35	37.08	35.90	34.65	85	42.98	41.90	40.80	39.75
40	38.95	37.78	36.61	35.31	90	43.41	42.41	41.32	40.30
45	39.35	38.31	37.06	35.85	95	43.85	42.90	41.85	40.78
50	39.85	38.76	37.58	36.39					



Fusion curve and surface tension isotherms in the system aniline-acetic acid.

As was shown earlier [4], in the system urea-acetic acid the surface tension isotherms are convex to the axis of composition, which indicates dissociation of the associated compound. In the system acetamide-acetic acid [5] the surface tension increases smoothly in passing from acid to acetamide. The isotherms are slightly convex to the axis of composition, which fact points to the occurrence in the homogeneous dilute medium of stronger chemical interaction. In the system aniline-acetic acid the surface tension isotherms have a sharp discontinuity and indicate the existence of a still more stable compound in the melt.

SUMMARY

1. The surface tension in the system aniline-acetic acid was investigated. The surface tension isotherms confirmed the existence of a compound in this system in a diluted medium.

2. A comparison of the surface tension isotherms of the systems $CH_3COOH-CO(NH_2)_2$, $CH_3COOH-CH_3CONH_2$, $CH_3COOH-C_6H_5NH_2$ shows that the stability of the compounds in melts increases in that order.

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INVESTIGATION OF COMPLEX FORMATION IN SOLUTIONS OF TERNARY SYSTEMS BY THE METHODS OF PHYSICO-CHEMICAL ANALYSIS

VIII. SYSTEMS $AlBr_3$-$(C_2H_5)_2O$-C_6H_5Cl, $AlBr_3$-$(C_2H_5)_2O$-C_6H_5Br AND $AlBr_3$-$(C_2H_5)_2O$-C_2H_5Br

E. Ya. Gorenbein and V. N. Danilova

The school of V. A. Plotnikov [1] investigated complex compounds of aluminum halides with halides of other metals by two main routes: 1) Synthesis of electrolytes for solvents with a low dielectric constant which can be classed as non-ionizable [2], and 2) electrolytic separation from non-aqueous solutions of metals which cannot be separated from aqueous solutions of electrolytes. These investigations showed that complex compounds of aluminum bromide with bromides of other metals are good electrolytes both for inorganic [3] and organic solvents [1, 4] with low dielectric constant (DC). Moreover, it was shown that some metals can be separated from solutions of complex compounds of aluminum bromide in organic solvents, but electrolysis is hindered by the instability of the solutions.

It should be noted that in spite of the great mass of experimental data for the formation of conductive solutions in solvents with low DC, some authors [5] even now adhere to antiquated concepts of the "dissociating power" of solvents.

With the objective of preparing stable solutions of complex compounds of aluminum halides, we decided to study the reaction of aluminum halides with ethers in various non-aqueous media by the methods of physico-chemical analysis.

In the present communication we present the results of an investigation of the viscosity, electrical conductivity and density of three systems:

$$AlBr_3\text{-}(C_2H_5)_2O\text{-}C_6H_5Cl,\ \ AlBr_3\text{-}(C_2H_5)_2O\text{-}C_6H_5Br \text{ and } AlBr_3\text{-}(C_2H_5)_2O\text{-}C_2H_5Br$$

at temperatures of 15, 20 and 25°.

EXPERIMENTAL

The solvents (ethyl bromide, chlorobenzene and bromobenzene) were thoroughly purified and dried over fused calcium chloride, distilled twice, and collected in drawn-out test tubes which were thereupon sealed. Preparations distilling within one degree were taken in the work. The purification of diethyl ether and the preparation of aluminum bromide have been described earlier [6].

Solutions were prepared in a conical flask with a side tube and ground-glass stopper. At first the fused aluminum bromide was poured in and weighed; then the appropriate solvent was added, followed (with cooling) by the ether. The quantity of solvent necessary for obtaining the required molar ratio of components was added with a small buret [7] and checked by weighing. The solution was poured into a cell for measurement of electrical conductivity, into a viscometer of the type described by A. I. Shatenshtein [8] and into a pycnometer [4]. Measurements were made in the apparatus previously described [9].

System $AlBr_3$-$(C_2H_5)_2O$-C_6H_5Cl

Chlorobenzene solutions of aluminum bromide are substantially non-conductive. Addition of ether to the solutions renders them conductive.

Some authors [10] report that aluminum bromide forms one compound with diethyl ether, while others report formation of two compounds [11]. The number may depend upon the nature of the solvent in which the aluminum bromide interacts with the ether.

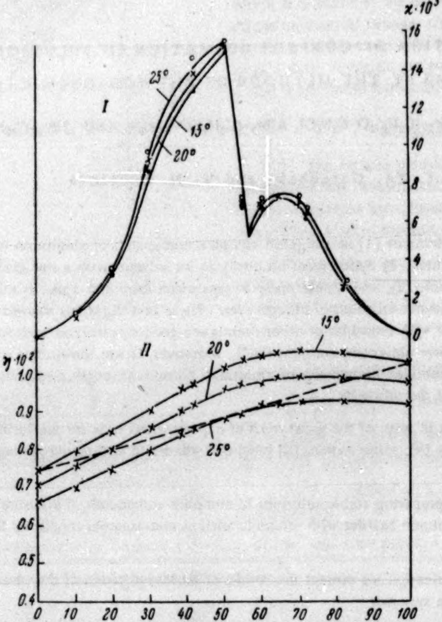


Fig. 1. Dependence of the specific electrical conductivity (I) and the viscosity (II) of the system $AlBr_3$-$(C_2H_5)_2O$-C_6H_5Cl on the ratio of $AlBr_3$ and $(C_2H_5)_2O$ in solution.

Solutions of aluminum bromide in chlorobenzene have a yellow color. Addition of ether causes the solution to turn paler, and the color disappears when there is an equimolar ratio of aluminum bromide to ether. The process of dissolution of ether in the chlorobenzene solution of aluminum bromide is accompanied by a considerable thermal effect, and the solution sometimes darkens if the ether is added quickly. The ether was therefore added dropwise to the system. We worked with perfectly transparent solutions. Fresh solution was prepared for each experiment.

In Table 1 are presented the data for a temperature of 15° only; the remaining data are shown graphically. Figure 1 shows the dependence of the specific electrical conductivity (I) and the viscosity (II) of the system on the ratio of concentrations of $AlBr_3$ and $(C_2H_5)_2O$, the total number of gram-molecules of which was assumed to be 100%.

TABLE 1

System $AlBr_3$-$(C_2H_5)_2O$-C_6H_5Cl

$\frac{M_{AlBr_3} + M_{(C_2H_5)_2O}}{M_{C_6H_5Cl}}$	$AlBr_3$ (mole %)	d_4^{15}	$\eta \cdot 10^2$	$\varkappa \cdot 10^6$
0.1499	0	1.0654	0.741	
0.1441	10.47	1.0909	0.795	0.96
0.1502	19.87	1.1197	0.846	3.34
0.1482	30.21	1.1467	0.904	8.76
0.1494	38.85	1.1690	0.962	—
0.1498	42.25	1.1838	0.970	13.08
0.1498	50.04	1.2001	1.015	14.91
0.1500	55.08	1.2121	1.029	6.95
0.1482	57.38	—	—	5.22
0.1498	60.35	1.2248	1.042	7.17
0.1510	64.58	1.2366	1.056	7.38
0.1497	70.24	1.2500	1.056	7.02
0.1465	72.26	—	—	6.31
0.1499	82.45	1.2808	1.051	2.55
0.1498	100	1.3234	1.028	—

The curve of specific electrical conductivity (Fig. 1) contains two maxima, the first corresponding to the compound $AlBr_3 \cdot (C_2H_5)_2O$ and the second to the compound $Al_2Br_6 \cdot (C_2H_5)_2O$. With rising temperature, the specific electrical conductivity increases slightly. There is a weak maximum on the curves of viscosity; the largest deviation from the additive straight line approximately corresponds to the compound $AlBr_3 \cdot (C_2H_5)_2O$, i. e. it coincides with the first maximum of specific electrical conductivity. Rise of temperature lowers the viscosity of the system and the maximum becomes less prominent.

System $AlBr_3$-$(C_2H_5)_2O$-C_6H_5Br

Solutions of aluminum bromide in bromobenzene do not conduct the electric current. Slight heating occurs when aluminum bromide is dissolved in bromobenzene. The solution turns red and sometimes becomes turbid but the turbidity disappears after addition of ether. With increasing concentration of ether the color of the solution changes from bright-red to cherry-red. The change of color corresponds to approximately equimolar ratio of $AlBr_3$ to $(C_2H_5)_2O$. In course of time the solutions with a higher content of aluminum bromide acquire a dark cherry-red color; the color of the solution does not change if ether predominates in the mixture.

Interaction of aluminum bromide with diethyl ether in bromobenzene solution is accompanied by a considerable thermal effect. The system is unstable; measurements of electrical conductivity, viscosity and density of the solutions were therefore carried out after the passage of equal intervals of time after mixing of the components.

Only data for a temperature of 15° are presented in Tables 2 and 3.

The specific electrical conductivity curve of the system (Fig. 2) contains two maxima and one minimum. The first maximum and the minimum correspond to one and the same compound – $AlBr_3 \cdot (C_2H_5)_2O$. The second maximum corresponds to the compound $Al_2Br_6 \cdot (C_2H_5)_2O$.

The viscosity increases with rising concentration of $AlBr_3$; the inflection on the curve corresponds to the second maximum of specific electrical conductivity. The maximum deviation of the curves from the additive straight line indicates formation in solution of the compound $Al_2Br_6 \cdot (C_2H_5)_2O$.

The present system does not conform to the rule that if two substances form two or more electrolytes, the viscosity curves will reflect that compound which has the highest electrical conductivity [12]. This may be associated with the differing stabilities of the compounds in the system.

TABLE 2

System $AlBr_3$-$(C_2H_5)_2O$-C_6H_5Br

$\frac{M_{AlBr_3}+M_{(C_2H_5)_2O}}{M_{C_6H_5Br}}$	$AlBr_3$ (mole-%)	d_4^{15}	$\eta \cdot 10^2$	$\frac{M_{AlBr_3}+M_{(C_2H_5)_2O}}{M_{C_6H_5Br}}$	$AlBr_3$ (mole-%)	d_4^{15}	$\eta \cdot 10^2$
0.1530	0	1.4190	1.021	0.1501	67.07	1.6020	1.539
0.1488	20.78	1.4740	1.181	0.1495	79.66	1.6270	1.519
0.1495	33.44	1.5070	—	0.1497	88.40	1.6406	1.520
0.1500	49.77	1.5612	1.420	0.1500	100	1.6692	1.520
0.1500	60.36	1.5810	1.507				

TABLE 3

$\frac{M_{AlBr_3}+M_{(C_2H_5)_2O}}{M_{C_2H_5Br}}$	$AlBr_3$ (mole-%)	$\varkappa \cdot 10^4$	$\frac{M_{AlBr_3}+M_{(C_2H_5)_2O}}{M_{C_2H_5Br}}$	$AlBr_3$ (mole-%)	$\varkappa \cdot 10^4$	$\frac{M_{AlBr_3}+M_{(C_2H_5)_2O}}{M_{C_2H_5Br}}$	$AlBr_3$ (mole-%)	$\varkappa \cdot 10^4$
0.1530	0	—	0.1500	49.77	9.42	0.1505	64.88	13.35
0.1490	14.24	3.08	0.1498	52.20	7.19	0.1503	71.64	9.26
0.1488	20.78	4.55	0.1501	53.65	10.24	0.1495	79.66	3.75
0.1494	43.12	14.56	0.1494	57.01	12.69	0.1497	88.40	1.41
0.1501	45.19	17.63	0.1582	58.63	13.35	0.1500	100	—
0.1497	49.16	20.16	0.1424	63.97	13.66			

System $AlBr_3$-$(C_2H_5)_2O$-C_2H_5Br

As already pointed out, neither bromobenzene nor chlorobenzene form solutions with $AlBr_3$ that conduct current. If ethyl ether is added to these solutions, the systems become conductive. We have seen that the development of conductivity is associated with the formation of conductive complexes.

It was of interest to study the effect of ether on a system in which one of the components forms a conductive solution with the solvent. Solutions with good conductivity are formed by aluminum bromide with ethyl bromide [13]. These components form the compound $AlBr_3 \cdot C_2H_5Br$ [14].

Dissolution of ethyl ether in an ethyl bromide solution of aluminum bromide is accompanied by a considerable thermal effect. The system was therefore cooled during addition of the ether. The solution of $AlBr_3$ in C_2H_5Br is straw-colored. It becomes brown when ether is added; on attainment of equimolar ratio of $AlBr_3$ to $(C_2H_5)_2O$, the color changes sharply and becomes colorless. The color changes from straw to brown in the interval of concentrations from 30 to 48 mole-% $(C_2H_5)_2O$. In this interval the electrical conductivity gradually increases with passage of time (it nearly doubles in 24 hours); this change can be neglected, however, after $1^1/_2$-2 hours (duration of an experiment). No change of electrical conductivity of other mixtures was observed after 24 hours. Results of investigations at 15° are given in Table 4.

Figure 3 shows that with increasing concentration of $AlBr_3$ the specific electrical conductivity at first rises and then falls sharply, passes through a minimum and again rises to the specific electrical conductivity of the binary system $AlBr_3$-C_2H_5Br. Neither the maximum nor the minimum of electrical conductivity corresponds to the exact composition of the compound formed in this system. Here the equimolar composition of the compound corresponds to the instant of abrupt transition of the electrical conductivity from maximum to minimum.

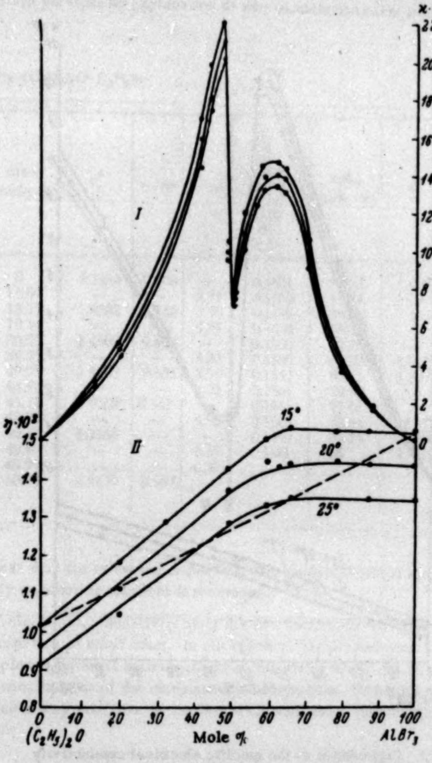


Fig. 2. Dependence of the specific electrical conductivity (I) and of the viscosity (II) of the system $AlBr_3$-$(C_2H_5)_2O$-C_6H_5Br on the ratio of $AlBr_3$ to $(C_2H_5)_2O$ in solution.

The binary system $AlBr_3$-C_2H_5Br differs from the systems discussed above in being electrically conductive. This behavior may be associated with the presence of only one maximum on the specific electrical conductivity curve (Fig. 3); there is no second maximum because the electrical conductivity of the binary system is probably higher than that of the complex formed.

Rise of temperature appreciably increases the electrical conductivity in the region of higher concentration of aluminum bromide for the ternary system and for the binary system $AlBr_3$-C_2H_5Br.

The viscosity increases with rising concentration of $AlBr_3$; the inflection point on the curve corresponds to the compound $AlBr_3 \cdot (C_2H_5)_2O$.

Measurements of density in all of the three systems are plotted in Fig. 4. The intersection of the branches starting initially from the densities of the binary systems corresponds to equimolar composition of the compounds formed in solution independently of which solvent is the medium for interaction between $AlBr_3$ and $(C_2H_5)_2O$. The

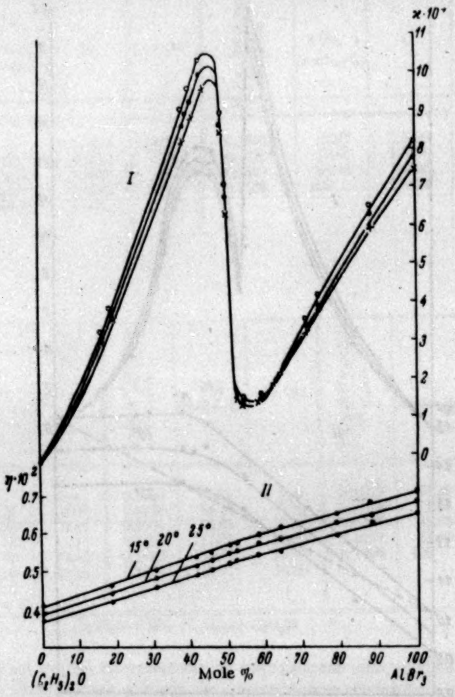


Fig. 3. Dependence of the specific electrical conductivity (I) and viscosity (II) of the system $AlBr_3$-$(C_2H_5)_2O$-C_2H_5Br on the ratio of $AlBr_3$ to $(C_2H_5)_2O$ in solution.

only difference is that the curves representing the dependence of densities on concentration of components in the systems $AlBr_3$-$(C_2H_5)_2O$-C_6H_5Br and $AlBr_3$-$(C_2H_5)_2O$-C_6H_5Cl are slightly concave to the abscissas whereas the curves of the system $AlBr_3$-$(C_2H_5)_2O$-C_2H_5Br are convex to the abscissas.

EVALUATION OF RESULTS

The experimental data indicate that aluminum bromide forms two complex compounds with ethyl ether, both in chlorobenzene and in bromobenzene, with the compositions $AlBr_3 \cdot (C_2H_5)O$ and $Al_2Br_6 \cdot (C_2H_5)_2O$. One compound is formed in ethyl bromide: $AlBr_3 \cdot (C_2H_5)_2O$. Solutions of these complex compounds in solvents with low DC are good conductors of the electric current.

We have thus obtained confirmation of V. A. Plotnikov's statements that "the dielectric constant of a solvent can never characterize the 'dissociating power' of a solvent if the influence of the dielectric constant is considered solely in conjunction with electric attraction according to Coulomb's law" [15], and that "the dielectric constant has significance only when ions are present; it regulates the interaction between the ions, but the dielectric constant provides no explanation of why dissociation takes place" [16].

TABLE 4

System $AlBr_3$-$(C_2H_5)_2O$-C_2H_5Br

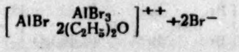
$\frac{M_{AlBr_3}+M_{(C_2H_5)_2O}}{M_{C_2H_5Br}}$	$AlBr_3$ (mole %)	d_4^{15}	$\eta \cdot 10^2$	$\varkappa \cdot 10^4$	$\frac{M_{AlBr_3}+M_{(C_2H_5)_2O}}{M_{C_2H_5Br}}$	$AlBr_3$ (mole %)	d_4^{15}	$\eta \cdot 10^2$	$\varkappa \cdot 10^4$
0.1503	0	1.3480	0.408	—	0.1501	52.23	1.5290	0.572	1.89
0.1447	15.94	—	—	2.95	0.1500	54.44	1.5338	—	1.40
0.1500	18.15	1.4082	0.454	3.76	0.1495	58.38	1.5469	0.5989	1.41
0.1561	19.14	—	—	3.87	0.1500	58.72	—	—	1.42
0.1454	30.05	1.4509	0.498	—	0.1500	62.29	—	—	1.93
0.1500	39.25	—	—	8.30	0.1500	64.27	1.5637	0.607	2.29
0.1497	40.95	1.4865	0.535	8.94	0.1457	68.71	1.5766	—	—
0.1498	44.58	—	—	9.77	0.1501	70.99	—	—	3.28
0.1500	45.12	1.5060	0.541	—	0.1485	75.04	—	—	3.83
0.1501	48.77	—	—	8.53	0.1500	79.74	1.6197	0.646	—
0.1489	49.48	1.5130	—	—	0.1499	88.32	1.6600	0.669	6.01
0.1487	49.60	—	—	8.35	0.1501	100	1.7120	0.706	7.63
0.1486	49.99	—	—	6.39					
0.1445	50.44	1.5170	0.567	—					

It is perfectly clear that the inference drawn from the Nernst-Thomson law that solvents with low DC cannot form electrically conducting solutions is erroneous.

An abrupt fall of electrical conductivity after the first maximum was observed in the systems that we investigated with participation of ethyl ether. In our opinion, this phenomenon must be associated with change of structure of the complexes (internal rearrangement of the atoms in the compounds). It may be suggested that, in dependence of the concentration of the components, the etherates formed in solution change their composition and structure in such a way that prior to the first maximum the conductivity is caused by electrolytic dissociation of the complex

$$Al_2Br_6 \cdot 2(C_2H_5)_2O \rightleftarrows [AlBr_2 \cdot 2(C_2H_5)_2O][AlBr_4]\ [^{17}].$$

V. A. Plotnikov [18] assigns to this compound the structure



$$\left[AlBr \begin{matrix} AlBr_3 \\ 2(C_2H_5)_2O \end{matrix} \right]^{++} + 2Br^-$$

With further rise of concentration of aluminum bromide, the structure of the complex changes in accordance with the equation $[AlBr_2 2(C_2H_5)_2O]\ [AlBr_4] \rightleftharpoons 2[AlBr_3(C_2H_5)_2O]$; this process results in a sharp fall in electrical conductivity; the resultant nonelectrolyte reacts with aluminum bromide to form a new complex:

$$[AlBr_3 \cdot (C_2H_5)_2O] + AlBr_3 = Al_2Br_6 \cdot (C_2H_5)_2O.$$

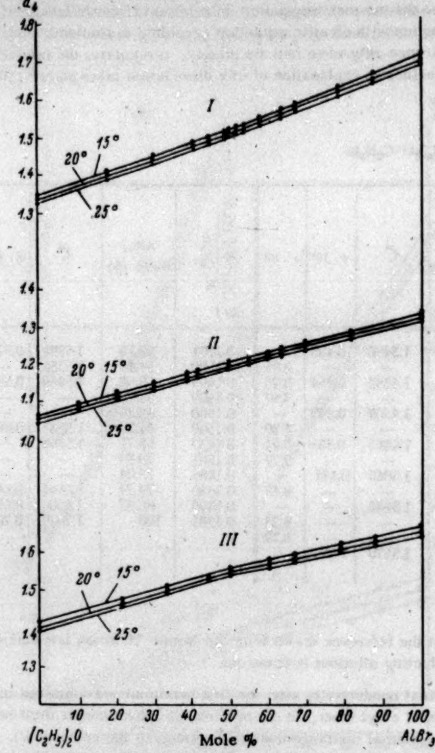
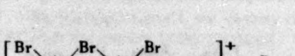


Fig. 4. Dependence of the density of the systems on the ratio of $AlBr_3$ to $(C_2H_5)_2O$ in solution.
I) $AlBr_3$-$(C_2H_5)_2O$-C_2H_5Br, II) $AlBr_3$-$(C_2H_5)_2O$-C_6H_5Cl, III) $AlBr_3$-$(C_2H_5)_2O$-C_6H_5Br.

This compound is an electrolyte which dissociates into ions:



$$\left[Br_2Al(\mu\text{-}Br)_2Al(Br)(C_2H_5)_2O \right]^+ + Br^-$$

The solvent might also enter into the composition of the compounds formed, but the data that we obtained do not allow of a definite conclusion on this problem.

SUMMARY

1. The interaction of aluminum bromide with ethyl ether was investigated in chlorobenzene, bromobenzene and ethyl bromide as solvents with isomolar concentration of components of 0.15 mole per mole of solvent, at temperatures of 15, 20 and 25°.

2. It was established that in chlorobenzene and bromobenzene aluminum bromide forms complex compounds with ethyl ether of the composition $AlBr_3 \cdot (C_2H_5)_2O$ and $Al_2Br_6 \cdot (C_2H_5)_2O$, whereas in ethyl bromide it forms one compound of the composition $AlBr_3 \cdot (C_2H_5)_2O$.

3. These solvents are good conductors of electricity in solvents with low DC.

4. It is shown that the inference from the Nernst-Thomson law that solvents with low DC cannot form electrically conductive solutions is erroneous.

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INVESTIGATION OF BINARY SYSTEMS OF BENZIDINE WITH PHENOLS AND NAPHTHOLS BY THE METHODS OF THERMAL ANALYSIS

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The aim of the investigation was to obtain further factual information in the field of interaction of the amino group of aromatic derivatives with acids, phenols, alcohols, etc. Studies of the interaction of aniline [1-4] and its homologs (alkarylamines [1, 3, 5-7]), toluidines [1, 3, 5, 8], etc. have been reported in the literature. Much less attention has been paid to the interaction of o-, m- and p-phenylenediamines [3, 9-11] or to amines with an amino group in a side chain not directly linked to the benzene ring.

Unlike the phenylenediamines, benzidine has two amino groups isolated from one another. The theory of the structure of organic compounds leads us to expect a reciprocal influence of the amino groups of benzidine.

EXPERIMENTAL

The visual-polythermal method was used in the investigation. The temperature of appearance of the first crystals and that of disappearance of the last crystals were noted with a specially calibrated thermometer accurate to 0.5°. The composition of the mixtures was calculated in molar percentages. Crystallization proceeded satisfactorily in the low-melting mixtures, but partial resinification of the products of fusion took place in high-melting mixtures; for some binary systems, therefore, the points were determined by the method of separate batches. The starting substances were thoroughly purified and their melting points were close to those in the literature. Since phenols and naphthols sublime, the components were melted in a test tube placed in a glass glycerol bath; the melts were vigorously stirred with a glass stirrer, and seeds were introduced.

1. System benzidine-phenol (Fig. 1, table). The eutectic from the phenol side runs nearly up to the ordinate (40°, 0.15% benzidine). The curve rises steeply at first and then descends to the eutectic point (113.5°, 77.5% benzidine). Benzidine forms with phenol an unstable compound of 1 : 2 composition, i. e. $(C_6H_4)_2(NH_2)_2 \cdot 2C_6H_5OH$.

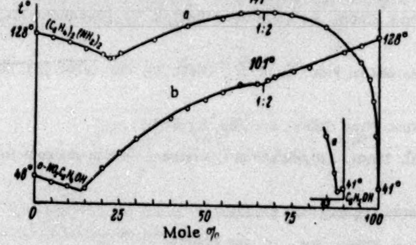

Fig. 1. Binary systems.
a) Benzidine-phenol; b) o-nitrophenol— benzidine.

Binary Systems of Benzidine With Phenols and Naphthols

C_6H_5OH (mole %)	Temperature	$C_6H_4(OH)_2$ (mole %)	Temperature	$C_6H_4(OH)_2$ (mole %)	Temperature	α-$C_{10}H_7OH$ (mole %)	Temperature	β-$C_{10}H_7OH$ (mole %)	Temperature	o-$NO_2C_6H_4OH$ (mole %)	Temperature
0	128.0°	0	128°	0	128.0°	0	128.0°	0	128.0°	0	128.0°
5	125.5	20	108.5	10	119.0	15	120.0	5	124.0	10	119.0
22	114.0	25	110.0	20	111.0	35	99.0	10	124.0	30	104.0
23	114.0	45	137.0	25	118.0	38	93.5	25	153.5	32	103.0
25	117.0	50	138.0	45	132.0	40	100.0	55	174.5	35	101.0
45	133.0	55	140.0	50	133.5	50	102.0	65	177.0	40	100.0
60	140.0	65	141.0	55	137.0	55	101.0	70	176.0	50	91.0
65	141.0	70	145.0	65	140.5	65	99.5	75	175.0	60	80.0
70	141.0	90	130.0	70	140.0	85	89.0	90	157.0	80	51.0
85	133.5	98.0	101.0	90	123.0	88	88.0	98	123.0	85	39.0
99.5	71.0	99	102.0	95	105.0	90	90.0	99	120.0	90	40.0
100	41.0	100	104.0	100	109.5	100	96.0	100	121.5	100	46.0

Note. The number of experimental points in the table has been reduced.

2. System benzidine-pyrocatechol (Fig. 2, table) forms a eutectic (105.5°, 77% benzidine); the liquidus curve then rises to 140° [unstable 1 : 1 compound, i. e. $(C_6H_4)_2(NH_2)_2 \cdot C_6H_4(OH)_2$], and then passes through a maximum at 145° corresponding to the compound $(C_6H_4)_2(NH_2)_2 \cdot 3C_6H_4(OH)_2$. The subsequent eutectic lies at 101° and 2% benzidine.

3. System benzidine-resorcinol (Fig. 2, table) forms a eutectic from the benzidine side (110°, 80.7% benzidine). The liquidus curve later rises to 132° (1 : 2 compound). A second liquidus lies at 105° and 5% benzidine. Benzidine forms two compounds with resorcinol: the unstable equimolar compound $(C_6H_4)_2(NH_2)_2 \cdot C_6H_4(OH)_2$ and $(C_6H_4)_2(NH_2)_2 \cdot 2C_6H_4(OH)_2$.

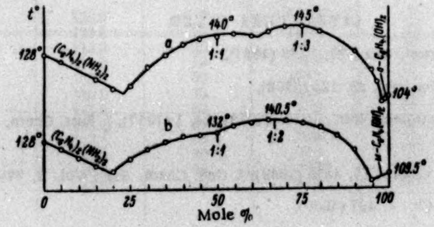

Fig. 2. Binary systems.
a) Benzidine-pyrocatechol; b) benzidine-resorcinol.

4. System benzidine-α-naphthol (Fig. 3, table). The liquidus curve has a very flat maximum at 1 : 1 composition. The eutectics lie at 93.5° and 63% and at 87° and 13.5% benzidine. The form of the curve indicates instability of the binary compound $(C_6H_4)_2(NH_2)_2 \cdot C_{10}H_7OH$. The melts are dark cherry-red.

5. System benzidine-β-naphthol (Fig. 3, table) forms a eutectic at 121° and 91.5% benzidine. The flat maximum of the curve lies at 172°; a second eutectic lies at 120° and 1% benzidine. The diagram points to formation of the unstable compound $(C_6H_4)_2(NH_2)_2 \cdot 2C_{10}H_7OH$. The melts have a blue color.

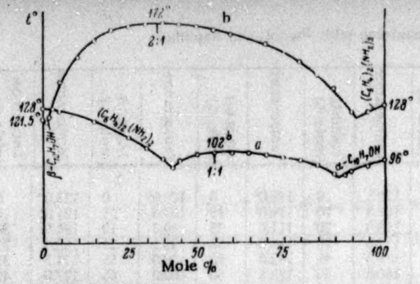

Fig. 3. Binary systems.
a) Benzidine—α-naphthol; b) β-naphthol—benzidine.

6. System benzidine—o-nitrophenol (Fig. 1, table) forms the very unstable compound $2(C_6H_4)_2(NH_2)_2 \cdot NO_2C_6H_4OH$ whose existence coincides with the transition point. The melts resinify with facility. The eutectic corresponds to 14.0% benzidine at 37°.

SUMMARY

Six binary systems formed by benzidine with mono- and dihydric phenols and with the naphthols were studied for the first time by the fusion method. Formation of the following compounds was established to a first approximation on the basis of analysis of the liquidus curves:

$(C_6H_4)_2(NH_2)_2 \cdot 2C_6H_5OH$,
$(C_6H_4)_2(NH_2)_2 \cdot o\text{-}C_6H_4(OH)_2$ & $(C_6H_4)_2(NH_2)_2 \cdot 3o\text{-}C_6H_4(OH)_2$,
$(C_6H_4)_2(NH_2)_2 \cdot m\text{-}C_6H_4(OH)_2$ & $(C_6H_4)_2(NH_2)_2 \cdot 2m\text{-}C_6H_4(OH)_2$,
$(C_6H_4)_2(NH_2)_2 \cdot \alpha\text{-}C_{10}H_7OH$ & $(C_6H_4)_2(NH_2)_2 \cdot 2\beta\text{-}C_{10}H_7OH$,
$2(C_6H_4)_2(NH_2)_2 \cdot o\text{-}NO_2C_6H_4OH$.

Introduction into phenol of a second hydroxy group (dihydric phenols) increases the tendency to complex formation, whereas the nitro group in the ortho position has a negative effect.

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THE TERNARY SYSTEM BENZIDINE-PHENOL-NAPHTHALENE

A. G. Bergman, A. P. Arestenko and A. I. Kislova

In the course of systematic study of the interaction of benzidine with acids, phenols, alcohols and other compounds, we have encountered difficulties due to the low thermal stability of the melts (partial decomposition occurs in some cases and resinification in others). Introduction of a third neutral component as a solvent affords the possibility of studying the interaction at lower temperatures and gives the opportunity of applying other methods of physico-chemical analysis.

Benzidine forms the compound $(C_6H_4)_2(NH_2)_2 \cdot 2C_6H_5OH$ with phenol (Fig. 1, Table 1). This is represented on the diagram by a curve with a relatively flat maximum at 141°. Both benzidine and phenol form eutectic systems with naphthalene without signs of complex formation (Fig. 1, Table 1). We therefore selected naphthalene as the neutral solvent.

TABLE 1

Binary systems*

$(C_6H_4)_2(NH_2)_2—C_6H_5OH$		$(C_6H_4)_2(NH_2)_2—C_{10}H_8$		$C_6H_5OH—C_{10}H_8$	
C_6H_5OH (mole %)	Temperature	$C_{10}H_8$(mole %)	Temperature	$C_{10}H_8$(mole %)	Temperature
0	128.0°	0	128.0°	0	41.0°
10	123.0	10	123.0	10	34.0
22	114.0	25	115.5	15	30.0
23	114.0	40	108.0	17.5	33.0
45	133.0	50	104.0	25	42.0
60	140.0	70	94.0	35	57.0
65	141.0	80	87.0	45	51.5
70	141.0	87	80.0	55	62.5
80	137.5	88	79.0	65	66.0
99.5	71.0	90	77.0	75	70.0
99.85	40.0	95	79.0	95	77.5
100	41.0	100	80.4	100	80.4

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* Not all of the experimental points are tabulated.

EXPERIMENTAL

The visual-polythermal method of investigation was used; temperatures were determined with a specially calibrated thermometer to an accuracy of 0.5°. The components were melted in a test tube placed in a glass bath containing glycerol. The melts were well-stirred with a glass stirrer; seed crystals were introduced. The substances were specially purified and had the constants reported in the literature. The composition of mixtures was calculated in mole-%.

Binary Systems

1. System benzidine-phenol was previously studied by us [1] (Fig. 1, Table 1). The eutectic from the phenol side is immediately at the ordinate (about 40° and 0.15% benzidine). The curve of the complex $(C_6H_4)_2(NH_2)_2 \cdot 2C_6H_5OH$ at first rises steeply from the phenol side, forms a flat maximum at 2 : 1 composition and slowly descends to the eutectic point at 113.5° and 22.5% phenol.

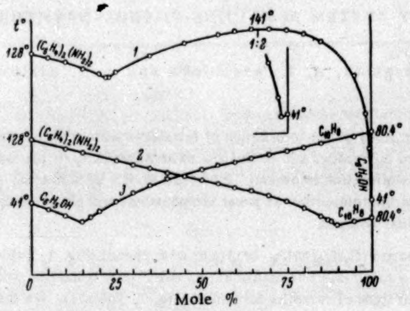

Fig. 1. Fusion diagram of binary systems.
1) $(C_6H_4)_2(NH_2)_2$-C_6H_5OH, 2) $(C_6H_4)_2(NH_2)_2$-$C_{10}H_8$, 3) C_6H_5OH-$C_{10}H_8$.

2. System benzidine-naphthalene (Fig. 1, Table 1) forms a eutectic at 77° and 10% benzidine.

3. System phenol-naphthalene. It is known that phenol does not form a compound with naphthalene, and the curve has the form of a simple eutectic [2-4]. We repeated the investigation and confirmed the general character of the system. The eutectic is at 30° and 15% naphthalene (Fig. 1, Table 1).

Ternary System

Nine cuts were investigated (Fig. 2, Table 2). On the basis of these data the fusion diagram of the ternary system was plotted (Figs. 3 and 4), the projection of which onto the phenol-naphthalene side is plotted in Fig.5.

The greater part of the surface of projection of the fusion diagram onto the triangle of composition (75.33%)* is occupied by the field of the compound $(C_6H_4)_2(NH_2)_2 \cdot 2C_6H_5OH$. The surface of crystallization has the form of a ridge extending to the eutectic point at a naphthalene content of 92% (Fig. 3). The benzidine field occupies 22.5%, the naphthalene field 2% and the phenol field 0.17%. A conspicuous feature is the increased curvature of the isotherms in the field of the compound with falling temperature, which indicates a decreased degree of dissociation in the melts. Of interest is the change of form of the isotherms in the benzidine field. The first isotherms are convex to the benzidine apex; the last ones are less convex and later become slightly concave.

The general appearance of the fusion diagram of the ternary system clearly reflects the inertness of naphthalene as a solvent towards the compound formed. The triangulating section VI, extending from the apex of the compound $(C_6H_4)_2(NH_2)_2 \cdot 2C_6H_5OH$ to the naphthalene apex divides the triangle into two ternary systems.

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* The binary compound of composition $(C_6H_4)_2(NH_2)_2 \cdot 2C_6H_5OH$ is designated by letter D on the diagram.

TABLE 2

Section I 50% C_6H_5OH+ +50% $C_{10}H_8$		Section II 25% C_6H_5OH+ +75% $C_{10}H_8$		Section III 10% C_6H_5OH+ +90% $C_{10}H_8$		Section IV 10% $(C_6H_4)_2(NH_2)_2$ + +90% C_6H_5OH		Section V 25% $(C_6H_4)_2(NH_2)_2$ + +75% C_6H_5OH		Section VI 33.3% $(C_6H_4)_2(NH_2)_2$+ +66.7% C_6H_5OH		Section VII 50% $(C_6H_4)_2(NH_2)_2$ + +50% C_6H_5OH		Section VIII 77.5% $(C_6H_4)_2(NH_2)_2$+ +22.5% C_6H_5OH		Section IX 90% $(C_6H_4)_2(NH_2)_2$+ +10% C_6H_5OH	
$(C_6H_4)_2(NH_2)_2$ (mole %)	Temperature	$(C_6H_4)_2(NH_2)_2$ (mole %)	Temperature	$(C_6H_4)_2(NH_2)_2$ (mole %)	Temperature	$C_{10}H_8$ (mole %)	Temperature	$C_{10}H_8$ (mole %)	Temperature	$C_{10}H_8$ (mole %)	Temperature	$C_{10}H_8$ (mole %)	Temperature	$C_{10}H_8$ (mole %)	Temperature	$C_{10}H_8$ (mole %)	Temperature
0	61.0°	0	72.0°	0	77.0°	0	127.0°	0	139.0°	0	141.0°	0	136.0°	0	114.0°	0	123.0°
0.1	60.0	**0.2**	**69.0**	0.5	77.0	5	125.0	5	137.0	10	137.0	10	132.0	5	112.0	5	120.0
0.15	**59.0**																
0.2	61.0	0.3	71.0	0.8	76.5	15	122.0	15	132.0	20	133.0	20	128.0	15	107.0	25	110.0
				0.9	**76.0**												
5	110.0	10	111.0	5	94.0	35	114.5	35	123.0	40	123.0	40	119.0	35	97.0	45	101.0
15	122.0	20	109.0	15	93.0	55	107.0	45	118.5	60	113.0	60	109.5	45	93.5	65	93.0
25	124.0	30	104.8	26	85.0	65	102.7	65	108.0	70	107.0	70	103.5	55	89.5	75	87.0
45	117.0	45	97.0	**27**	**84.0**	75	97.0	85	92.0	85	94.0	80	95.0	65	83.0	85	80.5
55	112.0	46	96.0	28	85.0	85	87.0	91	81.0	92	81.0	90	91.0	80	77.0	87	79.0
		46.5	**95.5**											**82.5**	**75.0**		
61	108.0	47	96.0	30	87.0	90	78.0	92	78.0	**93**	**79.0**	**92**	**77.0**	85	76.0	88	77.5
						91	**76.5**	**92.5**	**77.0**							**88.5**	**76.0**
63	106.0	55	102.0	60	107.0	94	77.0	94.5	78.0	94	79.5	93	77.5	90	78.0	90	77.0
63.5	**105.0**																
70	110.0	90	124.0	85	122.0	95	78.5	96	78.5	95	80.0	95	79.0	95	79.0	95	79.0
100	128.0	100	128.0	100	128.0	100	80.4	100	80.4	100	80.4	100	80.4	100	80.4	100	80.4

Note. A limited number of experimental points are included in the table; the eutectic temperatures and compositions are in bold type.

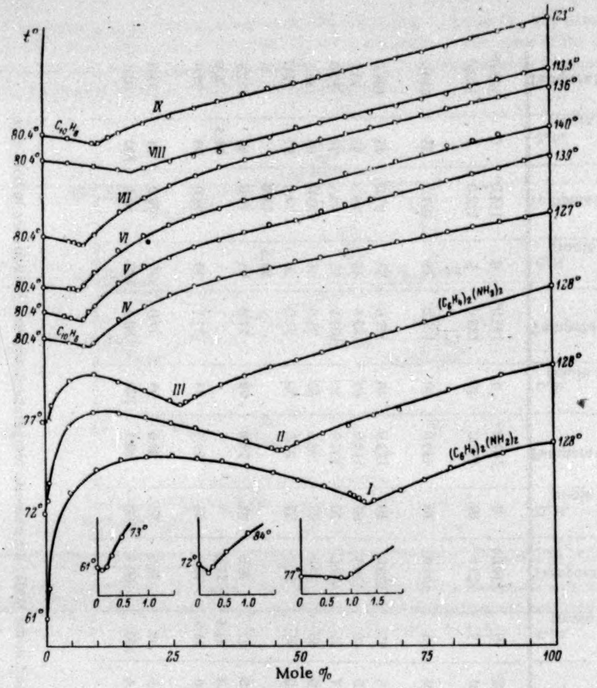

Fig. 2. Internal cuts of the ternary system.

I — 50% C_6H_5OH + 50% $C_{10}H_8$—$(C_6H_4)_2(NH_2)_2$, *II* — 25% C_6H_5OH + 75% $C_{10}H_8$—$(C_6H_4)_2(NH_2)_2$, *III* — 10% C_6H_5OH + 90% $C_{10}H_8$—$(C_6H_4)_2(NH_2)_2$, *IV* — $C_{10}H_8$—50% C_6H_5OH + 10% $(C_6H_4)_2(NH_2)_2$, *V* — $C_{10}H_8$—75% C_6H_5OH + 25% $(C_6H_4)_2(NH_2)_2$, *VI* — $C_{10}H_8$—66.7% C_6H_5OH + 32.3% $(C_6H_4)_2(NH_2)_2$, *VII* — $C_{10}H_8$—50% C_6H_5OH + 50% $(C_6H_4)_2(NH_2)_2$, *VIII* — $C_{10}H_8$—22.5% C_6H_5OH + 77.5% $(C_6H_4)_2(NH_2)_2$, *IX* — $C_{10}H_8$—10% C_6H_5OH + 90% $(C_6H_4)_2(NH_2)_2$.

A. Phenol-D-naphthalene with a ternary eutectic point located at 26° and corresponding to the composition 15% naphthalene, 0.5% benzidine and 84.5% phenol (Fig. 4). The ternary eutectic point E_1 slightly deviates on the fusion diagram from the eutectic point of the binary system phenol-naphthalene; this part of the triangle is therefore drawn on a larger scale.

B. Benzidine-D-naphthalene with a eutectic point E_2 located at 75° and corresponding to the composition 14% benzidine, 3.5% phenol and 82.5% naphthalene (Fig. 4).

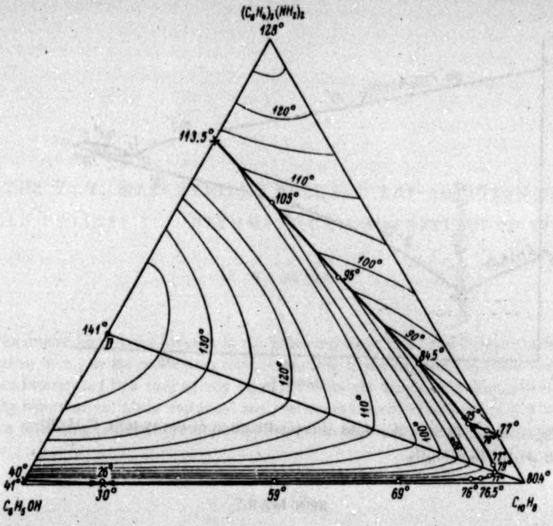

Fig. 3. Projection of the fusion diagram of the ternary system onto the triangle of compositions.

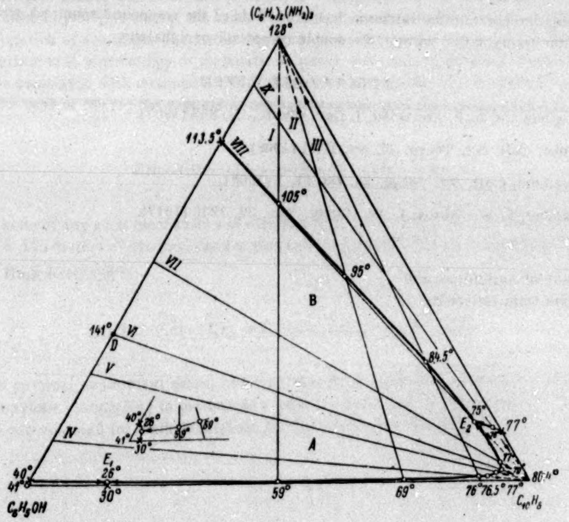
(C6H4)2(NH2)2
128°
IX
II
I
III
113.5°
VIII
105°
VII
95°
B
141°
VI
D
V
84.5°
40°
26°
59°
80°
41°
30°
IV
A
E2
75°
77°
77°
79°
E1
26°
40°
41°
30°
59°
69°
76°
76.5°
77°
80.4°
C6H5OH
C10H8

Fig. 4. Directions of the internal cuts in the ternary system.

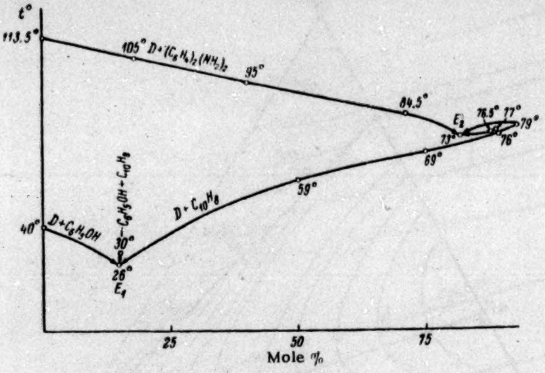

Fig. 5. Projection of the field of crystallization of the system C_6H_5OH-$(C_6H_4)_2(NH_2)_2$-$C_{10}H_8$.

SUMMARY

1. The ternary system benzidine-phenol-naphthalene was studied by the visual-polythermal method.

2. A definite maximum at 141° marks the formation of the compound $(C_6H_4)_2(NH_2)_2 \cdot 2C_6H_5OH$ which occupies 75.33% of the area of the triangle of compositions. The eutectic point corresponds to 93% naphthalene.

3. With falling temperature the isotherms inside the field of the compound acquire a greater curvature in the direction of the triangulating section: the double compound-naphthalene.

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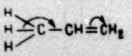
THE V. V. MARKOVNIKOV RULE FOR THE ADDITION OF HYDROGEN HALIDES TO UNSYMMETRICALLY SUBSTITUTED ETHYLENES

M. I. Batuev

V. V. Markovnikov formulated his rule in the following terms [1]: "The halogen adds on to the least hydrogenated carbon, i. e., to the one that is most susceptible to the influence of other reactants with carbon." This rule has been interpreted in a very widely accepted chemical theory of to-day, although this interpretation is on a purely hypothetical plane and lacks any precise and direct experimental confirmation. It has been suggested that the following (purely hypothetical) mechanism of electron shifts is applicable to propylene [2]:



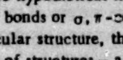
This is the M-effect – the decrease of the covalence developed by the outer carbon atom of the ethylenic group. The M-effect is said to be strengthened by the + T-effect of the methyl group whose C-H bond may be said to possess the ability to donate electrons, due to which its hydrogen atoms are protonized to a substantial extent. In another terminology of this theory, the same hypothetical mechanism of electron shift is called the statistical effect of conjugation of the single and double bonds or σ, π-conjugation (hyperconjugation of the first order). Using the polystructural terminology of molecular structure, the same hypothetical mechanism of electron shifts in propylene is associated with a combination of structures – a nonpolarized structure (I) and three polarized structures of the type of (II) (at the expense of the hydrogen atoms of the methyl group) [3].

$$\underset{\text{(I)}}{CH_3—CH=CH_2} \longleftrightarrow \underset{\text{(II)}}{H^+CH_2=CH—\bar{C}H_2}$$

On the basis of any such mechanisms of electron shift described by various terms and symbols, propylene also possesses a distribution of electron density that facilitates addition to it of hydrogen halides according to the rule of V. V. Markovnikov.

$$H_3C—\overset{\delta+}{C}H=\overset{\delta-}{C}H_2 + H^+ \mid Cl^- = H_3C—CHCl—CH_3$$

A direct physical experiment shows, however, that the hypothetical electronic mechanism does not actually apply to propylene. According to the concept under consideration, in propylene this mechanism is actually similar to the one proposed for methylacetylene (in this connection see [4]):



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just as in methylacetylene, this mechanism in propylene should also lead (due to the suggested protonization of the characteristic C-H bonds of the methyl group – the +T-effect) to a certain increase in the interatomic distance (r), to lowering of the energy (E) and of the frequency of the vibrations (ν); the same phenomena should also be observed in the characteristic $C = C$ bond due to the hypothetical reduction of its covalence by the end carbon atom (–M-effect). Actually, however, the opposite picture is observed in propylene (just as in acetylene): both the C-H bond of the methyl group and the $C = C$ bond are condensed ("electronized" [4]), i. e., their interatomic distance is shortened and the energy (E) and vibration frequency (ν) are increased. It suffices in this connection to cite the considerable increase of vibration frequencies of the bonds in question, since in the characteristic bonds the rise of vibration frequency is inevitably accompanied [4] by increase of bond energy and shortening of the interatomic distance [methylacetylene (Table 1) shown for comparison; cm^{-1}] [4, 5].

TABLE 1

Compounds	$C=C$	Compounds	CH_3*		Compounds	$C \equiv C$	Compounds	CH_3*	
			c	a				c	a
Propylene	1648	Propylene	2924	2987	Methylacetylene	2125	Methylacetylene	2927	2975
Ethylene	1621	n-Paraffins	2879	2938, 2867	Acetylene	1974	n-Paraffin	2879	2938, 2967
Rise	+27	Rise	+45	+34**	Rise	+151	Rise	+48	+22**

Consequently, in propylene and analogous compounds the hypothetical mechanism of electron shift implicit in the theory discussed is not a physical basis for the V. V. Markovnikov rule of addition; the hypothesis of the reality of this mechanism is refuted by exact physical experiment.

The primary physical factors governing the reciprocal influence of atoms in a molecule are the electron-nucleus interactions, as in a three-dimensional dynamic electron-nucleus system, the molecule existing in the given conditions in a state of definite labile equilibrium.*** At the present time, however, physical means do not enable us to fix the position of the bonding electrons in a molecule nor the position of the hydrogen atoms.**** However, electron-nucleus interactions in a molecule are clearly implicit in a whole series of its parameters, including the mechanical (vibration frequency ν), energy (bond energy E), geometrical (interatomic distance r), the direction of the changes of which is strictly defined for the characteristic bonds: rise of ν is always accompanied by increased E and shortening of r; fall in ν is accompanied by fall in E and rise in r. On the basis of the experimental data for these parameters, we can therefore unequivocally specify the physical state of the characteristic bonds – the change of their electron density,* their polarization,** etc. In the light of the considerations in this paper and the preceding one [4], we can now gain some insight into the physical state of the molecule of propylene, with reference to its individual bonds, as constituting a three-dimensional dynamic system in a condition of labile equilibrium which determines the course of the reaction of propylene with hydrogen halides in accordance with the V. V. Markovnikov rule.

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* Here and later c is symmetrical, a is antisymmetrical vibration.

** Relative to the mean of two frequencies of paraffins – frequency 2953 cm^{-1}.

*** We may note that A. M. Butlerov and his pupil V. V. Markovnikov developed the theory of chemical structure and of the reciprocal influence of atoms in a molecule as a truly existing dynamic network of atoms in which "we always find a state of specific labile equilibrium" [6]. They spoke of "... the totality of effects, both chemical and physical" in their fundamental inseparability in the molecule [7]. However, they clearly saw that physics lagged a long way behind chemistry in knowledge of the molecule (the concepts of bonds and structure). They stated: "... scanty knowledge of their (i.e. the physical factors') influence on the form of manifestation of chemical energy in each individual molecule" [8]. For this reason they said: "... at present we can only discuss the chemical influences since these are better known" [9], and they developed the theory of structure in its chemical aspect by chemical means, having in view the establishment of "... the order of the chemical bond between atoms in a molecule" [10], "... the arrangement of the chemical bond between the atoms" in a molecule [11], etc., but they referred to the integration of the chemical aspect with the physical aspect in the theory of structure as "... the future dynamic theory of chemistry" [12].

**** The Fourier method, with its limited possibilities in the x-ray structural analysis of crystals, determines the topographic distribution of the electron density but in no way satisfies the requirements of a theory of chemical structure in its physical aspect. An early solution of the problem of the position of the hydrogen atoms in a molecule can be expected mainly as a result of the development of neutronography.

The electronic density in the propylene molecule at the C-H bonds has a very irregular distribution. It is greatest in the methine and methylene groups, since these are located at the double C = C bond [4]; of the C-H bonds of these groups, the highest density is in the methylene, particularly in its antisymmetrical, vibrational state.*** The electron density in the C-H bonds of the methyl group is also increased but to a lesser extent than in CH and CH_2 (the hydrogen atoms of the C-H bonds of the methyl group are not directly joined to the double bond as in the methine and methylene groups, so that in propylene the influence of the double bond on the increase of frequencies of the C-H bonds in the methyl is lower than in the methine and methylene groups) (cm^{-1}) (Table 2).

TABLE 2

Compound	CH_3		CH	CH_2	
	s	a		s	a
Propylene	2924	2987	3002	3015	3086
Paraffins *	2879	2939, 2967	2870	2853	2908
Increase	+45	+32**	+132	+162	+178

* Frequencies of CH_2 and CH_3 according to data for normal paraffins, the frequency of CH according to data for branched paraffins.

** Relatively to the mean of the two frequencies of paraffins – a frequency of 2953 cm^{-1}.

As we have observed, the electron density of the double bond is also appreciably increased. In other words, all the C-H bonds of propylene are highly electronized, and especially the C-H bonds of the methylene group.

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* Under the influence of neighboring atoms and other structural factors, the electron density is distributed nonuniformly throughout the bonds: in the case of a shortened bond, for example, the electrons of the outer electron shell of the C and H atoms constituting the bond between these atoms, which are in constant orbital movement, execute this movement in a smaller space (and their effective density is greater) than in the case of a lengthened C-H bond, etc.

** This is discussed more fully in [4].

*** Without going into details, we may note that when there is an accumulation of C-H bonds at a carbon atom (for example on passing from the CH radical to methylene, or from the methyl groups of normal paraffins to methane), the interaction of the C-H bonds is intensified, and this leads to splitting of the frequency of the vibrations into the frequency of the symmetrical and the frequency of the antisymmetrical vibrations and to a raising of their total level, i. e., to intensification of their electronization (shortening of r, increase of ν and E) and to increase of their electron density (cm^{-1}).

Radical	CH	2824
n-Paraffins	CH_2	2853 s, 2908 a
	CH_3	2879 s, $\underbrace{2938,\ 2967}$ a
Methane	CH_4	2916 s, $\underbrace{3020,\ 3070}$ a

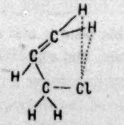
The molecule of a hydrogen halide is strongly polarized. This polarization if of course intensified when it approaches the C = C bond of propylene during reaction, becoming purely ionic H^+/Hal^-. Due to the negligibly small dimensions of the proton, to its great mobility* and its great affinity to the electron, it initiates the reaction which is preferentially directed into the region of the molecule with maximum electronic density (the region of the methylene group at the double bond); this results in rupture of the double bond, and the hydrogen halide attracts one of the electron pairs of the double bond. At a certain instant of time, the second carbon of the double bond (with the methine group) becomes positive and readily attracts and adds on the negative halogen ion. The stages of the addition reaction may be represented by the following scheme:

$$H_3C-CH=CH_2+H^+\ Cl^-=H_3C-\overset{+}{C}H-CH_3+Cl^-=H_3C-CHCl-CH_3$$

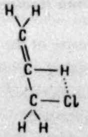
On replacing the methyl group by other alkyls, no fundamental changes are observed either in the distribution of the electron density (degree of electronization) of the bonds of the vinyl group or in the mode of addition of hydrogen halides. In vinyl chloride $CHCl = CH_2$, the strongly electronegative chlorine slightly weakens the C = C bond; however, the level of electronization of the C-H bonds of the methylene group remains high (higher than in the methine bond of C-H); addition of hydrogen halides proceeds in the usual order. Quite a different picture is observed, however, in allyl chloride: at low temperatures the mode of addition of hydrogen halides is contrary to the Markovnikov rule

$$ClH_2C-CH=CH_2+HCl=ClH_2C-CH_2-CH_2Cl$$

This deviation from the rule is caused by the rotational isomerism of allyl chloride. In the cis-isomer of allyl chloride, the interaction of the C-H bonds of the methylene group with the chlorine atom is extremely marked;** it leads to considerable weakening (protonization) of the C-H bonds of the methylene group; this effect is reflected in a fall in level of their vibrational frequencies (so that E is reduced and at the same time r is lengthened). The methine group of the cis-isomer, on the other hand, remains substantially electronized. Since at low temperatures the cis-isomer predominates in the mixture of rotational isomers of allyl chloride, the addition to it of hydrogen halides under these conditions naturally proceeds contrary to the Markovnikov rule.



Cis-isomer



Trans-isomer

In the trans-isomer (see structural formula above) the methinic C-H bond is protonized due to its interaction with the chlorine atom, whereas the C-H bonds of the methylene group are strongly electronized. The trans-isomer predominates in the mixture of isomers at normal or elevated temperature, and under these conditions the addition of hydrogen halides naturally proceeds in accordance with the Markovnikov rule (Table 3) [5].

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* In weak aqueous solutions at 25°, the lability of the hydrogen ion is 0.003624 and the lability of the chlorine ion is 0.000791 cm/sec with a potential gradient of 1 v/cm, i.e., the first is nearly five times more labile than the second [13].

** See the observations in [14] on the participation of the chlorine atom in the formation of hydrogen bonds and on the lowering of the frequencies of the O-H vibrations in O-H ... Cl.

TABLE 3

Frequencies of the C-H Bonds of the Cis- and Trans-Isomers of Allyl Chloride (cm^{-1})

Isomer	C-H bond of the methylene group	C-H bond of the methine group
Cis	2877, 2957	2989
Trans	3021, 3090	2877

We note that the frequency of the C-H bonds of the CH_2Cl group overlaps with the frequencies of 2989, 3021 cm^{-1}. Compared with the double bond of propylene (1648 cm^{-1}) the double bond of allyl chloride is very slightly weakened (1641 cm^{-1}), whereas that of vinyl chloride is much more weakened (1601 cm^{-1}).

SUMMARY

1. The validity of the Markovnikov rule in additions of hydrogen halides to unsymmetrically substituted ethylenes is not due to the occurrence in the latter of the hypothetical +T and –M effects (called also σ, π-conjugation or hyperconjugation of the first order), or to the combination of corresponding unpolarized and polarized structures, etc. The hypothesis of the occurrence of these effects in the ethylenes in question is refuted by exact physical experiment. Realization of the Markovnikov rule is governed by a definite (experimentally demonstrable), extremely irregular distribution of the electron density over the bonds in unsymmetrically substituted ethylenes, the latter constituting dynamic equilibrium systems of atoms. The reaction proceeds in definite stages.

2. The anomalous addition of hydrogen halides to allyl chloride is the consequence of the rotational isomerism of the latter.

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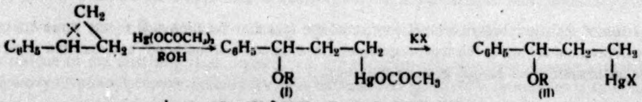
THE REACTION OF CYCLOPROPANE HYDROCARBONS WITH MERCURIC SALTS

VI. ORGANOMERCURY COMPOUNDS FROM PHENYLCYCLOPROPANE

R. Ya. Levina, V. N. Kostin, and V. A. Tartakovsky

The cleavage of the three-membered ring by the action of mercuric acetate has been studied by us earlier in the instance of various alkylcyclopropanes [1-3]. In the present work this reaction has been extended to the arylcyclopropanes; the reaction of mercuric acetate with phenylcyclopropane in aqueous and methanol solutions has been investigated.

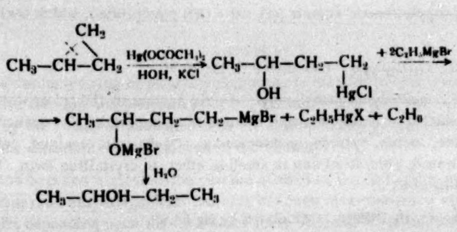


$$C_6H_5\text{—}\overset{CH_2}{CH\text{—}CH_2} \xrightarrow[ROH]{Hg(OCOCH_3)_2} \underset{(I)}{C_6H_5\text{—}\underset{OR}{CH}\text{—}CH_2\text{—}\underset{HgOCOCH_3}{CH_2}} \xrightarrow{KX} \underset{(II)}{C_6H_5\text{—}\underset{OR}{CH}\text{—}CH_2\text{—}\underset{HgX}{CH_2}}$$

where OR = OH & OCH_3; X = Cl, Br, I, CN, CNS

By this reaction a series of crystalline organomercury compounds was obtained that can be used for the identification of phenylcyclopropane.

To demonstrate the structure of the γ-mercurated alcohol-salts of 3-hydroxy-3-phenylpropylmercury obtained [(II) OR = OH], and consequently the place of cleavage of the three-membered ring in phenylcyclopropane, we employed a reaction replacing the HgCl group by MgBr, a method of reducing organomercury compounds [4] successfully used by us earlier [3] in studying the structure of the products of the reaction between mercuric acetate and alkylcyclopropanes.



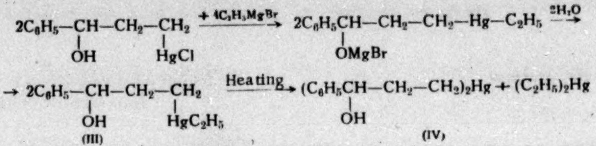
$$CH_3\text{—}\overset{CH_2}{CH\text{—}CH_2} \xrightarrow[HOH,\ KCl]{Hg(OCOCH_3)_2} CH_3\text{—}\underset{OH}{CH}\text{—}CH_2\text{—}\underset{HgCl}{CH_2} \xrightarrow{+2C_2H_5MgBr}$$

$$\longrightarrow CH_3\text{—}\underset{OMgBr}{CH}\text{—}CH_2\text{—}CH_2\text{—}MgBr + C_2H_5HgX + C_2H_6$$

$$\downarrow H_2O$$

$$CH_3\text{—}CHOH\text{—}CH_2\text{—}CH_3$$

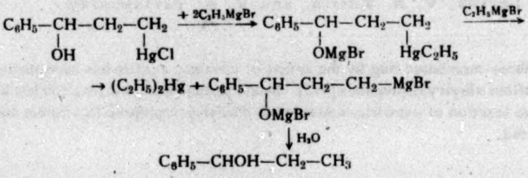
However, by the reaction under these conditions of 3-hydroxy-3-phenylpropylmercuric chloride [(II) OR = = OH; X = Cl] with ethylmagnesium bromide we obtained instead of the expected ethylphenylcarbinol a viscous, clear oil, which evidently was the completely substituted, unsymmetrical organomercury compound (III), since upon heating it broke down into diethylmercury and di-(3-hydroxy-3-phenylpropyl) mercury (IV).



$$2C_6H_5-\underset{OH}{CH}-CH_2-\underset{HgCl}{CH_2} \xrightarrow{+4C_2H_5MgBr} 2C_6H_5\underset{OMgBr}{CH}-CH_2-CH_2-Hg-C_2H_5 \xrightarrow{2H_2O}$$

$$\rightarrow \underset{(III)}{2C_6H_5-\underset{OH}{CH}-CH_2-\underset{HgC_2H_5}{CH_2}} \xrightarrow{Heating} \underset{(IV)}{(C_6H_5\underset{OH}{CH}-CH_2-CH_2)_2Hg} + (C_2H_5)_2Hg$$

Only when this reaction was carried out under more severe conditions (several hours of boiling with the Grignard reagent), was the expected phenylethylcarbinol obtained:



$$C_6H_5-\underset{OH}{CH}-CH_2-\underset{HgCl}{CH_2} \xrightarrow{+2C_2H_5MgBr} C_6H_5-\underset{OMgBr}{CH}-CH_2-\underset{HgC_2H_5}{CH_2} \xrightarrow{C_2H_5MgBr}$$

$$\rightarrow (C_2H_5)_2Hg + C_6H_5-\underset{OMgBr}{CH}-CH_2-CH_2-MgBr \xrightarrow{H_2O} C_6H_5-CHOH-CH_2-CH_3$$

The formation of the phenylethylcarbinol confirmed the fact that the cleavage of the three-membered ring in phenylcyclopropane occurs at the most highly polarized carbon-carbon bond (between the arylated carbon atom and an unsubstituted carbon atom of the ring).

EXPERIMENTAL

Phenylcyclopropane and mercuric acetate in aqueous solution. To a solution of 122 g of mercuric acetate in 430 ml of distilled water was added 45 g of phenylcyclopropane.

B. p. 54° at 10 mm, n_D^{20} 1.5350, d_4^{20} 0.9405. Previously reported [5]: b. p. 173° at 758 mm, n_D^{20} 1.5342, d_4^{20} 0.9401.

The reaction mixture was shaken for 12 hours at room temperature. Completion of the reaction was ascertained by the disappearance of the hydrocarbon layer. To the reaction product, which separated out as a heavy, colorless oil, were added ether extracts of the aqueous layer; the ether and acetic acid were distilled off in vacuo from the ethereal solution, and the residue was again dissolved in ether. Upon standing, coarse crystals of 3-hydroxy-3-phenylpropylmercuric acetate [(I), OR = OH] precipitated, which melted at 65-66°; yield 105 g (71%).

Found %: Hg 51.08, 50.83. $C_{11}H_{14}O_3Hg$. Calculated %: Hg 50.80.

Into a solution of 4.5 g of 3-hydroxy-3-phenylpropylmercuric acetate in 150 ml of water, cooled with ice, was poured, with constant stirring, a chilled aqueous solution of an equimolecular quantity of potassium chloride, or of potassium bromide, iodide, cyanide, or thiocyanate. Of the salts obtained, only the thiocyanate [(II) OR = OH; X = CNS] precipitated, after dissolving in absolute ether, in crystalline form. 3-Hydroxy-3-phenylpropylmercuric thiocyanate melted at 61°.

Found %: Hg 51.02, 50.59. $C_{10}H_{11}ONSHg$. Calculated %: Hg 50.93.

By the symmetrization of 3-hydroxy-3-phenylpropylmercuric acetate (by the action of an alkaline solution of sodium stannite [6]) di-(3-hydroxy-3-phenylpropyl)mercury also was obtained, m. p. 77-78° (recrystallized from aqueous acetone).

Found %: C 45.92, 46.05; H 4.95, 4.93. $C_{18}H_{22}O_2Hg$. Calculated %: C 45.93; H 4.71.

Phenylcyclopropane and mercuric acetate in methanol solution. A mixture of 27 g of mercuric acetate in 75 ml of anhydrous methyl alcohol with 10 g of phenylcyclopropane was shaken for 12 hours at room temperature. After distilling off the methyl alcohol and acetic acid in vacuo, 28 g (82%) of 3-methoxy-3-phenylpropylmercuric acetate [(I) OR = OCH_3] separated in the form of a non-crystallizing oil; by exchange reaction with potassium salts, crystalline organomercury compounds [(II), OR = OCH_3; X = Cl, Br, I, CN] were obtained, which were recrystallized from ether.

3-Methoxy-3-phenylpropylmercuric chloride m.p. 82°. Found %: Hg 51.96, 52.45. $C_{10}H_{13}OClHg$. Calculated %: Hg 52.07.

3-Methoxy-3-phenylpropylmercuric bromide m.p. 87°. Found %: Hg 46.27, 47.04. $C_{10}H_{13}OBrHg$. Calculated %: Hg 46.68.

3-Methoxy-3-phenylpropylmercuric iodide m. p. 79°. Found %: Hg 42.30, 42.12. $C_{10}H_{13}OIHg$. Calculated %: Hg 42.08.

3-Methoxy-3-phenylpropylmercuric cyanide m. p. 84°. Found %: Hg 47.50, 47.10. $C_{11}H_{13}ONHg$. Calculated %: Hg 47.67.[*]

Reaction of 3-hydroxy-3-phenylpropylmercuric chloride (II) with ethylmagnesium bromide. a) Reagent ratio 1 : 2 and boiling for 1 hour. An ether solution (1 : 2) of 30 g (0.08 mole) of 3-hydroxy-3-phenylpropylmercuric chloride was added drop by drop to an ether solution of ethylmagnesium bromide (3.9 g magnesium and 17.5 g, i. e. 0.16 mole, of ethyl bromide) with constant stirring. The reaction mixture was then stirred for 1 hour, while slowly boiling; hydrolysis was carried out with dilute acetic acid. The ether layer (together with ether extracts of the aqueous layer) was washed with a dilute alkali solution and dried with magnesium sulfate. After the ether was evaporated in vacuo, a viscous oil remained, apparently (3-hydroxy-3-phenylpropyl)-ethylmercury (III). Disproportionation of this fully substituted, unsymmetrical organomercury compound occurred when it was heated for a half-hour in vacuo (12 mm); 5.4 g (51%) of diethylmercury distilled off.

B. p. 51° at 12 mm, n_D^{20} 1.5400. Previously reported [7]: b. p. 57° at 16 mm, n_D^{20} 1.5399.

The residue in the distilling flask crystallized; after recrystallization from aqueous acetone, 9 g (47.5%) of di-(3-hydroxy-3-phenylpropyl) mercury (IV) was obtained, m. p. 77-78°. A mixture with a known sample of the compound obtained by the symmetrization of the corresponding mercuric acetate [(I), OR = OH] gave no depression of the melting point.

b) Reagent ratio 1 : 3 and boiling for 12 hours. An ether solution of 30 g (0.08 mole) of 3-hydroxy-3-phenylpropylmercuric chloride was added to an ether solution of ethylmagnesium bromide (6 g of magnesium and 27 g, i. e. 0.24 mole, of ethyl bromide) and the reaction mixture was boiled for 12 hours. After hydrolysis, the usual working up of the ether solution, and removal of the ether by distilling in vacuo, a very mobile liquid was obtained; from this were separated by distillation in vacuo: diethylmercury, b. p. 48° at 9 mm, n_D^{20} 1.5392, and ethylphenylcarbinol (5.4 g, 46%), b. p. 85° at 9 mm, n_D^{20} 1.5280. The 3,5-dinitrobenzoate prepared from the carbinol melted at 67-68°; a mixture with a known sample of the 3,5-dinitrobenzoate of ethylphenylcarbinol showed no depression of the melting point. Previously reported [8]: b.p. 131-132° at 50 mm; m. p. of dinitrobenzoate 68°.

SUMMARY

1. The three-membered ring of phenylcyclopropane is cleaved by the action of mercuric acetate in aqueous or methanolic solution and 3-hydroxy- or 3-methoxy-3-phenylpropylmercuric acetate is formed, from which are obtained by the action of potassium salts the corresponding gamma-mercurated alcohols or their methyl ethers with the different anions attached to the mercury.

2. The reaction between a gamma-mercurated alcohol of the indicated structure (3-hydroxy-3-phenylpropylmercuric chloride) and ethylmagnesium bromide has been investigated; it was shown that the reaction yields different results depending upon the conditions under which it is carried out, namely: a) with a reagent ratio of 1 : 2 and heating the reaction mixture for an hour, an exchange occurs between the anion (chlorine) in the organomercury compound and the ethyl group; the product of this reaction is the unsymmetrical, fully substituted organomercury compound (3-hydroxy-3-phenylpropyl)-ethylmercury; upon further heating in vacuo to 50°, disproportionation occurs, forming the two symmetrical compounds diethylmercury and di-(3-hydroxy-3-phenylpropyl)mercury; b) with a reagent ratio of 1 : 3 and 12 hours heating, the (3-hydroxy-3-phenylpropyl)-ethylmercury formed reacts further with the ethylmagnesium bromide to produce diethylmercury and ethylphenylcarbinol.

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[*] The corresponding thiocyanate was a non-crystalline oil.

3. The formation of the ethylphenylcarbinol is evidence of the structure of the gamma-mercurated alcohols obtained, and consequently of the place of cleavage of the three-membered ring in phenylcyclopropane – between the arylated and the unsubstituted carbon atoms.

4. For the first time crystalline organomercury compounds have been described which can serve for the identification of phenylcyclopropane: these are 3-hydroxy-3-phenylpropylmercuric acetate and the corresponding thiocyanate; 3-methoxy-3-phenylpropylmercuric chloride and the corresponding mercuric bromide, iodide and cyanide; and di-(3-hydroxy-3-phenylpropyl)mercury.

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RADICAL AND ION ALKYLATION OF THE AROMATIC NUCLEUS

IV. BENZYLATION OF GUAIACOL, TOLUENE, AND BENZENE

I. P. Tsukervanik and S. G. Melkanovitskaya

Continuing our work on the clarification of the possibility of radical alkylation of the aromatic nucleus and of the conditions necessary, we turned to the use of metallic copper as a catalyst. It was known that copper was a catalyst for typical radical reactions and in particular was used to obtain free triaryl radicals [1]. The use of copper as a catalyst for alkylation reactions, described by Zincke [2] and Gomberg [3], had been haphazard and had not been systematically studied.

A series of investigations has shown the possibility of benzylating the aromatic nucleus in the presence of zinc and aluminum [4], also titanium, cerium, uranium, and chromium [5].

We have investigated the possibility of benzylating benzene, toluene, guaiacol, benzaldehyde, and methyl benzoate by heating benzyl chloride with these aromatic compounds in the presence of a small amount of powdered copper.

It was known that it was possible to thermally benzylate naphthalene, diphenyl, anisole, mesitylene [6] and phenol [7]. We have shown that it is also possible to thermally benzylate guaiacol (at 200-210°), toluene (at 240-280°), and benzene (at 300-310°). In all cases of thermal benzylation studied by us or described in the literature, the reaction products are mono- and dibenzyl compounds; the formation of dibenzyl has not been observed.

In our first experiments we used freshly reduced copper, prepared from copper sulfate and zinc dust. In the condensations we observed strong evolution of HCl and partial conversion of the copper to Cu_2Cl_2. In special experiments it was ascertained that Cu_2Cl_2 under the given conditions did not catalyze at all the reactions being investigated. By polarographic analysis it was found that the copper catalyst that had been used contained about 0.5% zinc. In separate experiments with toluene we showed that with the amounts of zinc present in this alloy the yield of benzyltoluene did not exceed 14%, compared with 75.5% obtained under the same conditions with copper. In further work copper bronze powder was used (Kalbaum). Neither copper powder obtained by the reduction of CuO in a stream of hydrogen nor commercial copper powder (GOST 4960-49) washed with hydrochloric acid showed catalytic activity under the conditions described.

In the presence of small quantities of powdered, freshly reduced copper or copper bronze (0.1 gram-equiv.), benzylation of guaiacol, toluene, and benzene proceeded at low temperatures (80-90°) and gave good yields of the mono- and dibenzyl compounds (46-76%). When 0.6 gram-equivalent of a diluted catalyst (commercial copper powder with a small admixture of freshly reduced copper) was used for the benzylation of benzene, the main reaction product was dibenzyl (11-14%) with diphenylmethane as an impurity.

In experiments with benzaldehyde and methyl benzoate, benzylated products were not formed. A large amount of tarry material was formed by polymerization of benzyl chloride; in addition, in both instances a little dibenzyl was produced.

The data obtained show that the reaction activity of the aromatic compounds in both thermal and catalytic benzylation reactions falls into the series: guaiacol, toluene, benzene, methyl benzoate.

It must be noted that there is an inconsistency in the data in the literature on the reactivity of the benzyl radical. G. A. Razuvaev [8] and B. A. Dolgoplosk [9] observed only its dimerization; Kharasch [10] and Hickinbottom [11] reported benzylation of benzene, mesitylene, and quinoline.

We suppose that such inconsistencies are the result of the absence in the literature of a clear demarcation between free radical reactions and reactions proceeding with the homolytic redistribution of bonds but without the formation of independent particles. O. A. Reutov [12] has noted this circumstance.

In order to have a basis for relating the reactions studied to different groups, we examined the possibility of benzylation by azobenzil, which upon thermal decomposition yields free benzyl radicals [13]. The reaction between azobenzil and toluene in a sealed tube at 200-210° did not give benzylated products. Dibenzyl, stilbene, and a hydrocarbon melting at 179.5-180.5° were obtained. These same products were prepared by Waters [13] by the decomposition of azobenzil in decalin. Upon decomposition of azobenzil in nitrobenzene, which could act as an acceptor for hydrogen displaced from the aromatic nucleus by the benzyl radical, there were again no benzylated products detected. The main products recovered were aniline and stilbene.

These data lead us to the conclusion that neither catalytic nor thermal benzylation reactions with benzyl chloride take place through the medium of free radicals; a homolytic redistribution of bonds occurs within the reaction complex. In these reactions copper plays the role of a donor-acceptor of electrons.

EXPERIMENTAL

Thermal benzylation of guaiacol. 8.6 g of benzyl chloride and 8.2 g of guaiacol were heated for 8 hours. Evolution of HCl began at 185-186°. The temperature was slowly increased and at the end had reached 260°. The darkened, viscous mass was fractionated. After distilling off the unreacted guaiacol (2.3 g) we obtained: 3.15 g (21.6%) of benzylguaiacol, b. p. 195-208° at 23 mm; 1.3 g of a dark, viscous oil, b. p. 200-240° at 17-11 mm; from which was recovered dibenzylguaiacol; 5.8 g of a tarry residue.

Reaction in a sealed tube (200-210° for 8-9 hours) yielded 37.8% benzylguaiacol.

Benzylation of guaiacol in the presence of freshly reduced copper. 8.6 g of benzyl chloride, 8.2 g of guaiacol, and 0.43 g of copper were heated for 8 hours to 100-160°. Yield: 4.3 g (29.5%) of benzylguaiacol, 4.4 g (41.5%) of dibenzylguaiacol, 2.3 g of tarry residue. The dibenzylguaiacol fraction was a very viscous oil, which crystallized upon the addition of ether.

The benzylguaiacol after several redistillations had the following constants:

b.p. 200.5° at 25 mm, d_4^{20} 1.132, n^{20} 1.5886. MR_D 63.65; calc. 62.81.

Found %: C 78.31; H 6.55. $C_{14}H_{14}O_2$. Calculated %: C 78.47; H 6.59.

In the literature are described 6-benzyl-1,2-hydroxylmethoxybenzene, which is a crystalline substance, and a benzylguaiacol with the position of the benzyl group unknown which boils at 269-270° at 436 mm, d_{13}^{13} 1.1380 [14].

2 g of benzylguaiacol in 5 ml of pyridine was heated for 1 hour on the water bath with 4 ml of benzoyl chloride. Upon dilution of the mixture with water, an oil separated which after washing and drying in benzene solution yielded colorless crystals of the benzoate, m. p. 96.5-97.5° (from alcohol).

Found %: C 79.18; H 5.81. $C_{21}H_{18}O_3$. Calculated %: C 79.22; H 5.70.

Dibenzylguaiacol after several recrystallizations from alcohol melted at 107.5-108.5°.

Found %: C 83.4; H 6.52. $C_{21}H_{20}O_2$. Calculated %: C 83.41; H 6.41.

Thermal benzylation of toluene. 5.3 g of benzyl chloride and 21.6 g of toluene were heated for 8-9 hours to 240-280° in a sealed tube. When the tube was opened, much HCl was given off. After the excess toluene was distilled off, the mixture was fractionated in vacuo. Yield: 4.6 g (60.5%) of p-benzyltoluene, b. p. 141-145° at 15 mm; 1.2 g of a yellow oil, b. p. 210-220° at 13 mm; 0.6 g of tarry residue.

Benzylation of toluene in the presence of freshly reduced copper. 6.8 g of benzyl chloride, 51 g of toluene, and 0.35 g of copper were heated to boiling for 16 hours. Evolution of HCl began after 1.5-2 hours. Upon completion of the reaction the mixture was filtered off from the precipitate and fractionated. Yield: 7.4 g (75.5%)

of p-benzyltoluene, b. p. 143-145° at 15 mm; 1.3 g of tarry residue.

The precipitate was treated with a solution of sodium chloride to remove Cu_2Cl_2. There was an insoluble residue of 0.05 g of copper.

The p-benzyltoluene after distillation over metallic sodium had the following constants:

b.p. 146-147° at 18 mm, d_4^{20} 0.9922, n_D^{20} 1.5715.

Data in the literature: b.p. 144° at 16 mm, d^{18} 0.994, $n_D^{19.3}$ 1.5710 [15].

By oxidation with chromic mixture [16], p-benzoylbenzoic acid was obtained, m. p. 195.5-196.5°.

Thermal benzylation of benzene. 10.1 g of benzyl chloride and 14 g of benzene were heated to 300-310° in a glass test tube with a loosely fitting cap in an autoclave for 12-14 hours. When the autoclave was opened, a large amount of HCl was evolved; the reaction mass appeared largely resinified.

After distilling off the benzene, the following fractions were collected: 1.8 g (13.4%) of diphenylmethane, b. p. 250-255° at 728 mm; 0.8 g of a viscous oil, b.p. 270-335°; upon standing, crystals melting at 60-81° separated from this oil.

After four recrystallizations needles were obtained with m.p. 80-84°, agreeing in melting point with mixed crystals of o- and p-dibenzylbenzene [17]. 3.2 g of tarry residue.

Benzylation of benzene in the presence of freshly reduced copper. 6.8 g of benzyl chloride, 12.6 g of benzene, and 0.35 g of copper were heated to boiling for 12 hours. Evolution of HCl began in 30-40 minutes; by the end of the reaction almost all the copper had been converted to Cu_2Cl_2. To remove the latter the reaction mixture was washed with sodium chloride solution, then with water, and dried with calcium chloride. Unreacted copper remained only on the walls of the flask. Yield: 2 g (22%) of diphenylmethane, b. p. 150-158° at 33-35 mm; 0.9 g of oil, b.p. 190-230° at 10 mm. From this oil crystals separated which appeared to be a mixture of o- and p-dibenzylbenzene; 0.7 g of tarry residue.

Benzylation of benzene in the presence of copper bronze powder. 20.4 g of benzyl chloride, 38 g of benzene, and 2.1 g of copper were heated to boiling for 12 hours. Evolution of HCl began as soon as the mixture started to boil. At the end of the reaction the mixture was filtered off from the precipitate and fractionated. Yield: 7.5 g (27.6%) of diphenylmethane, b.p. 255-263°; 4.1 g (19.7%) of a mixture of o- and p-dibenzylbenzene, b.p. 210-234° at 11 mm and m.p. 54-77°, from which was separated p-dibenzylbenzene, m.p. 84-86°, and o-dibenzylbenzene, m.p. 75-78° [17]; 4.6 g of a viscous, colored oil, b.p. 280-310° at 8 mm; 13.4 g of tarry residue.

The diphenylmethane after two distillations over metallic sodium had the following constants:

b.p. 147-148° at 29 mm, d_4^{20} 1.006, n_D^{20} 1.5750. MR_D 55.17; calc. 55.032.

Data in the literature: b.p. 141° at 27 mm, d_{25}^{25} 1.0056, n_D^{17} 1.5788 [18]. By nitration with nitric acid [19] (d 1.5) 4,4'-dinitrodiphenylmethane was obtained, m.p. 181-183°. Mixed melting point with a known sample 180.5-183.5°.

p-Dibenzylbenzene, m.p. 84-86°, was oxidized to p-dibenzoylbenzene, m.p. 160-162°.

o-Dibenzylbenzene, m.p. 75-78°, was oxidized to o-dibenzoylbenzene, m.p. 145-148° [20].

Benzyl chloride and methyl benzoate. 18 g of benzyl chloride, 21.5 g of methyl benzoate, and 4.2 g of copper were heated for 2 hours to 125-130°. Evolution of HCl began at 125°. At the end of the reaction the Cu_2Cl_2 was washed out with a solution of sodium chloride and the residual unreacted copper (0.5 g) was filtered off. After the unreacted materials (18 g) were distilled off, the following products were obtained: 0.7 g of crystals, 2.8 g of a viscous oil, and 5.5 g of tarry residue. The crystals appeared to be a mixture of dibenzyl and benzoic acid. Pure dibenzyl, m.p. 51-52°, was obtained by treatment of the mixture with a 20% sodium carbonate solution. Benzoic acid, m.p. 120-122°, was recovered from the sodium carbonate solution.

When benzaldehyde and benzyl chloride were reacted in an analogous manner, a little dibenzyl and benzoic acid, and a large amount of tar were again obtained.

Decomposition of azobenzil in toluene. Azobenzil was prepared from benzalazine [21] by reduction with sodium amalgam to dibenzylhydrazine [22] and oxidation of the hydrochloride of the latter with hydrogen peroxide [23]. 3.5 g of freshly prepared azobenzil (m.p. 32-34°) and 8.5 g of toluene were heated for 9 hours in a sealed tube to 200-210°. When the tube was opened, gaseous products were given off; among them ammonia was detected qualitatively. By fractionation of the reaction mixture the following were obtained: dibenzyl, m.p. 50-53°; stilbene, m.p. 120-124°; and a substance with m.p. 179.5-180.5°, for which Waters [13] has given the formula $C_{28}H_{26}$.

Decomposition of azobenzil in nitrobenzene. 9.2 g of freshly prepared azobenzil and 54.3 g of nitrobenzene were heated in an atmosphere of nitrogen at 145-155° for 12-13 hours. At the end of the reaction the mixture was heated to 198-204°. Yield: 1.7 g of aniline: stilbene, m.p. 120-124°; and an insignificant amount of crystals of m.p. 161-163°.

SUMMARY

1. Thermal benzylation of guaiacol, toluene, and benzene has been accomplished.

2. It has been shown that in the presence of small amounts of copper, benzylation of these compounds takes place at 80-90°; yield of products 46-76%.

3. Thermal decomposition of azobenzil in toluene or nitrobenzene solutions gives only products of dimerization and disproportionation of the benzyl radical.

4. It is considered that the benzylation reactions with benzyl chloride which are under consideration proceed as homolytic reactions, without formation of free radicals.

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CONDENSATIONS OF 1,4-BROMOCHLOROBUTANE WITH BENZENE

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When an aromatic nucleus is alkylated by dihalogen compounds in which the halogen atoms are located on widely separated carbon atoms, we might expect a stepwise reaction process:

$$ArH + X(CH_2)_nX \rightarrow Ar(CH_2)_nX \xrightarrow{+ArH} Ar(CH_2)_nAr.$$

However, the intermediate aralkyl halides usually cannot be isolated because of the ease with which further condensation and secondary reduction processes occur.

In our laboratory we have shown previously [1] that it is possible to obtain appreciable yields of gamma-bromopropylbenzene from 1,3-bromochloropropane and benzene under mild conditions (6 to 13°). Under ordinary conditions this reaction produces 1,3-diphenylpropane and n-propylbenzene. Continuing our investigations in this field, we have studied the alkylation of benzene by 1,4-bromochlorobutane.

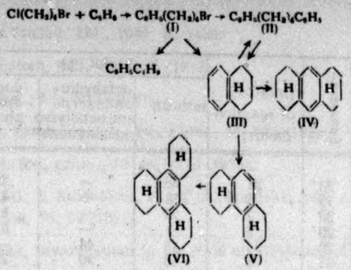
According to the data of Japanese chemists [2] condensation of 1,4-dichlorobutane with benzene in the presence of $AlCl_3$ yields tetralin. Somewhat earlier it was recorded in a patent [3] that reaction of benzene (16 moles), 1,4-dichlorobutane (6 moles), and $AlCl_3$ (1.2 moles) at 30 to 80° produced tetralin, 1,4-diphenylbutane (II), octahydroanthracene (IV), octahydrophenanthrene (V), and dodecahydrotriphenylene (VI). The last-named substance was the chief product; according to the data presented, it was formed in 28% yield. The yields of the other materials were low (2.5 to 10%).

Braun [4] has shown that delta-chlorobutylbenzene in the presence of $AlCl_3$ is very readily cyclized to tetralin. On the other hand, Schroeter [5] studied the action of $AlCl_3$ on tetralin and found among the products the above-mentioned compounds IV, V, and VI.

Boedtker [6] confirmed these data, determining that alkylation of tetralin in the presence of $AlCl_3$ always yields as by-products octahydroanthracene (IV) and octahydrophenanthrene (V). He also demonstrated the reversibility of such reactions by obtaining tetralin from benzene and dodecahydrotriphenylene (VI) with $AlCl_3$.

Barbot [7] found that tetralin with an excess of benzene gives 1,4-diphenylbutane. He considered this reaction a condensation of the intermediate delta-chlorobutylbenzene with benzene. V. V. Korshak et al. [8] reported the great ease with which 1,4-diphenylbutane is converted to tetralin as a reason for the failure to obtain reticulate polymers from ethyl polyphenylene and 1,4-dibromobutane.

On the basis of the data presented in the literature we anticipated the following possible paths for the condensation of 1,4-bromochlorobutane with benzene.



In undertaking our investigation, the purpose was to ascertain whether differences could be observed in the activity of the chlorine and bromine atoms in 1,4-chlorobromobutane, and whether the intermediate delta-bromobutylbenzene could be isolated. On the other hand it was necessary to clarify the influence of easy intramolecular cyclization on the general course of the alkylation.

The condensations were carried out with varying proportions of the reagents and different amounts of $AlCl_3$, at various temperatures and for different lengths of time. In no case did we succeed in obtaining delta-bromobutylbenzene (I), butylbenzene, or 1,4-diphenylbutane (II). Even with a very large excess of benzene (25 moles) and 0.1 mole of $AlCl_3$ at 20°, tetralin and compounds IV, V, and VI resulted. The maximum yield of tetralin was 65% and dodecahydrotriphenylene (VI) was simultaneously formed in 32% yield. When the amount of benzene was decreased, the proportion of these two products was changed. With 8 moles of benzene, 60% of dodecahydrotriphenylene (VI) and 20% of tetralin were obtained. Finally, an experiment carried out in petroleum ether solution with a 1 : 1 molar ratio of the reagents and 0.1 mole of $AlCl_3$ yielded only dodecahydrotriphenylene (65%); however, under these conditions almost half of the 1,4-bromochlorobutane was recovered unchanged.

These results clearly show that the condensation always proceeds through tetralin, which is converted into dodecahydrotriphenylene (VI) by further alkylation, and not at the expense of destructive processes as stated by Schroeter [5].

The use of increased amounts of $AlCl_3$(1 g-mole)promoted the formation of octahydroanthracene (IV) and octahydrophenanthrene (V). In experiments carried out at 75°, a mixture of all four compounds was obtained in a total yield near theoretical.

We attempted to make 1,4-diphenylbutane by Barbot's method [7] of heating a mixture of synthetic tetralin with an excess of benzene and $AlCl_3$ for 8 hours at 80°. After treatment in the usual manner, about 70% of unchanged tetralin was recovered and a little octahydrophenanthrene was isolated.

Thus in condensations of 1,4-bromochlorobutane with benzene the ease of formation of the six-membered ring determines the whole course of the process. An unusual result is the absence not only of 1,4-diphenylbutane, but also of butylbenzene, which can be easily obtained by the reduction of delta-bromobutylbenzene with simultaneous dehydrogenation of the cyclohexane nuclei of compounds IV, V and VI. Such a conversion has been observed in many alkylation reactions with di- and polyhalogenated compounds [9]. We do not exclude, however, the possibility of changing the course of the condensations under consideration by altering the conditions or selecting other aromatic compounds.

EXPERIMENTAL

1,4-Bromochlorobutane was prepared from tetrahydrofuran by way of 4-chlorobutanol-1 [10]. A preparation was used which boiled at 80-82° at 30 mm, n_D^{20} 1.5938, d_4^{20} 1.4898.

The condensations were carried out by gradually adding $AlCl_3$ to a solution of 1,4-bromochlorobutane in benzene. The mixture was stirred continuously during the reaction at constant temperature. After the usual treatment and removal of excess benzene, the crude products were fractionated in vacuo. The residue remaining after distilling off the tetralin frequently started to crystallize.

The results of several typical experiments are given in the table.

Experiment No.	Molar ratio 1,5• -bromochlorobutane: benzene: $AlCl_3$	Temperature	Duration of reaction (hours)	Yields (%)		
				tetralin	octahydroanthracene and octahydrophenanthrene	dodecahydrotriphenylene
1	1 : 25 : 0.1	20°	24	65	—	30
2	1 : 13 : 0.1	75	4	31	—	43
3	1 : 8 : 0.1	20	3	22	—	62
4	1 : 1.3 : 0.1	20	5	—	—	65••
5	1 : 25 : 1	20	24	43	44	—
6	1 : 25 : 1•••	75	4	50	20	20

• As in original. 1,4 was probably intended – Publisher's note.

•• In petroleum ether solution (100 ml). Recovered 65% of the 1,4-bromochlorobutane.

••• Moist $AlCl_3$.

The following hydrocarbons were obtained as products of the reactions:

Tetralin [11]. B. p. 200° (730 mm), n_D^{17} 1.5452, d_4^{17} 0.9690.

The perbromide melted at 182-183°. Dehydrogenation of the crude material at 160-180° yielded naphthalene, m. p. 79-80°, no depression of m. p. when mixed with a known sample.

Octahydroanthracene [12]. Colorless, lustrous crystals, m. p. 70.5-71° (from alcohol). Benzene solutions had a blue fluorescence. Dehydrogenation with selenium at 280-300° yielded anthracene, m. p. 206-208°, identical with a known sample.

Octahydrophenanthrene [13]. Fluorescent oil. B. p. 290° (730 mm), n_D^{17} 1.5663, d_4^{20} 1.0360.

Dehydrogenation with selenium at 170-220° yielded phenanthrene, m. p. 89-91°; no depression of m. p. when mixed with a known sample. Besides phenanthrene, a little anthracene was obtained from the dehydrogenation.

Dodecahydrotriphenylene [14]. Crystallized from a mixture of alcohol and benzene as long, yellowish needles. Colorless after sublimation. M. p. 226-228°. Dehydrogenation with selenium in a sealed tube at 320-360° yielded triphenylene, m. p. 195-196° after sublimation [15]. By oxidation of dodecahydrotriphenylene with nitric acid (d 1.53) in a sealed tube at 160-180°, mellitic acid was obtained, m. p. 287°.

For direct comparison, dodecahydrotriphenylene was synthesized from cyclohexanone and sulfuric acid [16]. The preparations were identical.

SUMMARY

1. In condensations of 1,4-bromochlorobutane with benzene in the presence of $AlCl_3$, the products are tetralin, dodecahydrotriphenylene, octahydroanthracene, and octahydrophenanthrene.

2. Yields of these compounds depend chiefly upon the proportion of the reagents. With a large excess of benzene, 65% tetralin is obtained. With insufficient benzene, only dodecahydrotriphenylene (65%) is formed.

3. Because of the great ease of formation of new six-membered rings under the conditions of condensation studied, it was not possible to isolate delta-bromobutylbenzene, butylbenzene, or 1,4-diphenylbutane.

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DETERMINATION OF THE ACTIVITY OF ORGANIC COMPOUNDS CONTAINING RADIOACTIVE CARBON C^{14}

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In the determination of the activity of compounds containing in their composition the radioactive isotope of carbon with mass number 14, use is generally made of end-window counters with a thin mica window. Use of the end-window counter requires that the specimen for the count be in the form of a solid material, usually barium carbonate, spread in a thin layer on the support. Work with the end-window counter is associated with a number of difficulties. Trouble arises from the relatively low counting efficiency and the difficulties encountered in the preparation of specimens of uniform composition with an even surface. In the determination of the activity of organic compounds labeled with radiocarbon, further complications arise in the ignition of the specimens and the preparation of the barium carbonate precipitate; the direct determination of the activity of organic compounds labeled with radiocarbon C^{14} by introducing them into the counter is thus an attractive proposition.

A number of authors [1-3] have suggested methods for the determination of the activity of specimens, labeled with C^{14}, in the form of carbon dioxide introduced directly into a counter with internal loading; carbon disulfide is recommended as a quenching agent. The latter is, however, inconvenient in use since it is capable of dissolving in the valve lubricant. In addition, the vacuum apparatus suggested in the above works for filling the counter with the gas mixture is too complex and inconvenient for everyday use. There are reports [4, 5] that ethyl alcohol vapor may be used as quenching agent in these experiments.

In a work by ourselves and B. V. Aivazov [6], a description is given of the simple construction of a vacuum apparatus for filling the counter with a gas mixture and the results are recorded of studies on the possibility of determining the activity of specimens, containing in their composition radiocarbon C^{14}, in the form of carbon dioxide. The vapors of alcohols, hydrocarbons, alkyl halides and other organic compounds were used as quenching agents. National standard counting tubes and apparatus were used in the work. The tests showed that results could be obtained using counters with copper cathodes. Counters of this type give a plateau extending over approximately 350 V with a slight gradient amounting to approximately 0.5%.

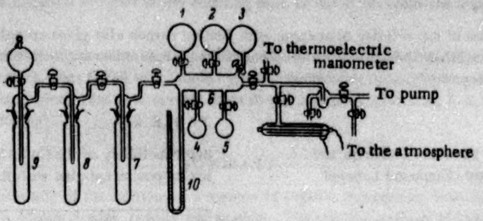
From the different organic compounds tested by us, an excellent quenching action was shown by ethyl alcohol vapor, whose concentration may amount to from 20 to 50% of the carbon dioxide pressure. A horizontal plateau of 250-300 V may be obtained for counters containing hexane or heptane vapors in amounts of from 30 to 70% of the total pressure. Ethyl bromide and acetone vapor may also be used as quenching agents in the carbon dioxide.

In the present work a description is given of the results of studies on the determination of the activity of organic compounds labeled with C^{14} and introduced directly into a Geiger-Muller counter.

The direct determination of the activity of organic compounds labeled with radiocarbon has considerable advantages over counting methods using solid specimens or carbon dioxide.

EXPERIMENTAL

A vacuum apparatus, whose general outline is given in the diagram, was chosen for the study.



Vacuum apparatus for the determination of the activity of specimens, labeled with radiocarbon, in a counter with internal loading. Explanation in the text.

Carbon dioxide or argon was chosen as the main gas for filling the counter tube. The carbon dioxide was prepared from a carbonate and sulfuric acid in tube 9, purified by freezing in traps 7 and 8 and collected in flasks 1 and 2. Flask 3 contained the argon, while flasks 4 and 5 contained the vapor of the organic compounds whose activity was to be determined. The manometer 10 was used to prepare mixtures of the required composition and to measure the pressure in the counting tube. A special cathetometer was used to increase the accuracy of the pressure readings on the manometer.

Standard counting tubes with copper cathode and tungsten anode were used as counters. The counting tube was sealed by a special side-arm to the vacuum apparatus and enclosed in a lead castle.

The vacuum system was evacuated to a pressure of the order of 10^{-2} mm mercury using a vacuum pump. Before the measurements, the counting tube was heated with a stream of warm air with continued evacuation. A mixture of the required composition was then washed through and the tube filled for measurement of the count rate.

The materials chosen for study were labeled ethyl acetate, ethyl propionate, ethyl butyrate, acetone, acetaldehyde, acetic acid, benzene and certain other compounds.

For each organic compound labeled with radiocarbon C^{14}, measurements were made of the length and gradient of the characteristic count plateau with varying composition of the mixture introduced into the counter. In addition, the relationship between the count rate and the quantity of labeled organic compound introduced into the counter was measured. All the measurements were repeated many times, with different samples of a mixture of a given composition. This allowed the reproducibility of the results obtained to be assessed.

All the measurements were carried out over a period of time sufficient to give a statistical error of not more than 1%. Calculation of the accuracy of counting, the error in reading the pressure and other errors showed that the error of our determinations of labeled organic compounds in a counter with internal loading is of the order of 2%.

It follows from the experiments carried out that determination of the activity of ethyl acetate labeled with radiocarbon is possible with concentrations of from 10 to 40% of the vapor of the latter in the count mixture. The main gas used here was carbon dioxide or argon. With a concentration of approximately 40% of the ester in the count mixture, the length of the plateau was approximately 200 V with a gradient of the order of 0.1%, while with 10% of the ester it was 125 V with a gradient of the order of 3.0%.

Ethyl propionate with the carbon of the carboxyl group labeled can be introduced into the counter in amounts of from 10 to 25% of the total pressure. The highest value for the length of the horizontal plateau was observed for 15-20% ester.

Ethyl butyrate and acetic acid have a relatively low vapor pressure at room temperature, which makes it difficult to introduce them into the counter in high concentrations. We were able to obtain quite satisfactory reproducible results in work with the counter using 10-12% of labeled ethyl butyrate or labeled acetic acid vapor in the counter.

The determination of the activity of acetone with labeled carbon also gives completely satisfactory results. The excellent reproducibility and low gradient of the plateau make it possible to determine the labeled acetone with an accuracy of ±3%.

TABLE 1

The Relationship Between Count Rate and Pressure of Organic Compound Labeled with Radiocarbon

Pressure (in mm Hg)			Count rate (imp./min.)	Impulses/min. for 1 mm Hg pressure of the compound
Organic Compound	CO_2	total		
Acetic acid				
6	54	70•	240	40
7	53	70•	280	40
8	52	70•	320	40
9	51	70•	369	41
Acetone				
30	40	70	1300	40
50	20	70	2050	41
70	—	70	2800	40
Ethyl acetate				
6	54	60	1860	310
8	52	60	2496	312
10	50	60	3090	309
12	48	60	3636	303
Ethyl propionate				
8	52	60	1851	231
10	56	60	2300	230
12	48	60	2688	224
Ethyl butyrate				
8	52	60	1176	147
10	50	60	1479	148

TABLE 2

Reproducibility of the Count Rate of Organic Compounds Labeled with Radiocarbon

Count rate (impulses/minute)	Impulses/min. for 1 mm Hg pressure of the compound
Ethyl butyrate (6mm) + CO_2 (54 mm)	
882	147
900	150
889	148
894	149
888	149
Ethyl propionate (10mm) + CO_2 (50mm)	
2311	231
2289	228
2310	231
2300	230
2300	230

The activity of labeled acetaldehyde was determined by us with quantities of the latter introduced into the counter up to 30% of the total pressure. The working characteristics of the counter had a plateau length of 100-150 V approximately, with a gradient of approximately 2%.

In all these measurements, except for the experiments with acetic acid, the labeled compounds were at the same time quenching agents.

The activity count of acetic acid labeled with radiocarbon requires the introduction of ethyl alcohol vapor into the counting tube as a quenching agent.

Measurement of the relationship between the count rate and the partial pressure of the labeled organic compound showed that there is a linear relationship between these two quantities. This can easily be seen from the data in Table 1.

We carried out special experiments to study the reproducibility of the results obtained. In these experiments the counting tube was filled several times with a count mixture of a given composition. Measurement of the count rate was carried out each time under identical conditions.

The results obtained for some of the compounds studied are given in Table 2.

• Ethyl alcohol vapor to a pressure of 10 mm mercury was added for the determinations.

The data in Table 2 indicate sufficiently high reproducibility. Separate measurements carried out under identical conditions with different samples in the counting tube do not differ from one another by more than 2-3%.

We studied the stability of operation of the counters with time for mixtures of different composition. It was established that counting tubes filled with labeled organic compounds mixed with carbon dioxide or argon give a practically unaltered count rate over several hours of uninterrupted operation, i. e. their operation is sufficiently stable with time.

SUMMARY

The direct determination of the activity of a number of organic compounds, labeled with radiocarbon, by direct introduction into a counting tube, is fully practicable. The relative activity of esters, hydrocarbons, acetone and a number of other ketones, acetaldehyde, alkyl halides, etc., can be determined with completely satisfactory accuracy.

Carbon dioxide or argon may be used as working gas for filling the tube. When carbon dioxide is used, the working voltage of the counting tube is slightly higher than when argon is used.

To improve the operation of the counters in those cases where the quenching action of the labeled organic compound is insufficient, ethyl alcohol vapor should be introduced into the counting tube in amounts up to 10-20% of the total pressure.

An accuracy of ± 2.0% may be reached in the determination by the method given.

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CATALYTIC REACTIONS IN THE PRESENCE OF METALLIC ALUMINUM

III. ALKYLATION OF CHLOROBENZENE BY ETHYL BROMIDE, n-PROPYL BROMIDE, AND n-BUTYL BROMIDE

M. B. Turova-Polyak and M. A. Maslova

The possibility of alkylating halogenated benzenes, in particular chlorobenzene, with alkyl halides in the presence of metallic aluminum has not previously been investigated.

As a result of our investigations it has been possible to show that the reaction between chlorobenzene and ethyl, n-propyl, or n-butyl bromide in the presence of metallic aluminum (under the conditions recommended by Azatyan [1] proceeds very energetically and is completed in a few minutes, with satisfactory yields of the alkylchlorobenzenes. The rule developed by us [2] for the alkylation of benzene by alkyl halides is confirmed in this case: the yields of alkylchlorobenzenes rise with increasing molecular weight of the alkyl halide. In this work it also was established that the yields of the alkylation products depend upon the composition of the reaction mixture: the best yield of ethyl chlorobenzene (46.6%) was obtained with a 3 : 1 ratio of chlorobenzene to ethyl bromide; the best yields of propylchlorobenzene (59.2%) and butylchlorobenzene (69.1%) were obtained with a 5 : 1 ratio of the corresponding components. The alkylation of chlorobenzene with n-propyl bromide and n-butyl bromide yielded isopropyl- and butylchlorobenzenes of undetermined structure. Polyalkylchlorobenzenes were not obtained under our experimental conditions.

The comparatively high yields of alkylchlorobenzenes indicate that the use of metallic aluminum as a catalyst for this reaction is fully justified. This is especially so if we keep in mind that carrying out the reaction, as well as separating the alkylation products, is considerably easier than with other catalysts, particularly aluminum chloride.

EXPERIMENTAL

The starting materials, which were carefully dried and distilled immediately before the experiment, had constants agreeing with the literature.

A mixture of chlorobenzene, the bromo-derivative, and freshly cut aluminum turnings was slowly heated on an oil bath until the reaction started, which could be determined by a change in color of the solution and the appearance of bubbles of hydrogen bromide. When chlorobenzene was alkylated with ethyl bromide, the reaction started in 40-60 minutes after the mixture began to boil; when the alkylation was carried out with n-propyl bromide or n-butyl bromide, it started in 10-15 minutes after boiling began. The reaction, when it started, immediately became very vigorous and was accompanied by copious evolution of hydrogen bromide and a simultaneous drop in the temperature of the reaction mixture of 20-25°. When this occurred, heating was stopped and the reaction continued energetically and was completed in a few minutes. The reaction mixture was then heated again on the water bath for another 30-40 minutes. The reaction products constituted a homogeneous, mobile, transparent, red-brown liquid. All the experiments were carried out with 0.01 gram-atom of aluminum per mole of halogen derivatives [2]. Data on the effect of the composition of the reaction mixture on the yield of alkylation products are given in table 1.

After each experiment the alkylation products were separated with acidified water, carefully washed, dried, and repeatedly distilled. The first distillation separated the excess chlorobenzene and a broad fraction

TABLE 1

Molar ratio benzene: alkyl bromide	Yields (%)		
	ethylchlorobenzene	propylchlorobenzene	butylchlorobenzene
1 : 1	36.0	34.0	30.8
2 : 1	38.3	41.0	40.0
3 : 1	46.6	46.2	48.9
4 : 1	43.8	52.7	58.3
5 : 1	42.7	59.2	69.1
6 : 1	33.2	53.2	62.9
7 : 1	28.2	45.7	56.6

corresponding to the alkylchlorobenzenes. Repeated distillations yielded fractions with constants close to those of the individual alkylchlorobenzenes. The position of the alkyl groups in the alkylation products was determined by oxidation of the latter with nitric acid (d 1.2) [3]. According to the data in the literature o-chlorobenzoic acid melts at 140.65° [4], m-chlorobenzoic acid at 157.5° [5], and p-chlorobenzoic acid at 239° [4].

In tables 2 to 4 data are given for the distillation of the ethyl-, propyl-, and butylchlorobenzene fractions from those experiments in which the largest yields of alkylation products were obtained, together with the melting points of the oxidation products and, for comparison, the constants of the individual alkylchlorobenzenes.

TABLE 2

Fractions and ethylchlorobenzenes	Amount (wt. %)	Boiling point at 760 mm	n_D^{20}	d_4^{20}	MR_D^*	Melting point of oxidation products
1st	14.5	176.5—178°	1.5192	1.0440	40.86	192—194°
2d	18.8	178 —179	1.5193	1.0440	40.86	—
3rd	9.1	179 —180	1.5192	1.0450	40.80	—
4th	52.9	180 —184.5	1.5191	1.0440	40.85	201
Residue	0.7	—				
Loss	4.0	—				
Ethylchlorobenzenes						
ortho [6]		178.4	1.5217	1.0569		
meta [6]		183.7	1.5194	1.0529		
para [6]		184.4	1.5175	1.0455		

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* Calculated for C_8H_9Cl, MR_D 40.41.

From a comparison of the constants of the alkylation products (especially the specific gravities in tables 2 to 4) and the melting points of the oxidation products with the constants given in the literature for the corresponding compounds, it appears that the p-alkylchlorobenzenes predominate in the products of alkylation of chlorobenzene with alkyl bromides.

TABLE 3

Fractions and isopropylchlorobenzenes	Amount (wt. %)	Boiling point at 760 mm	n_D^{20}	d_4^{20}	MR_D^*	Melting point of oxidation products
1st	28.6	190 —191.5°	1.5145	1.0340	45.01	200°
2d	32.3	191.5—192.5	1.5138	1.0290	45.15	—
3rd	31.4	192.5—196	1.5131	1.0250	45.32	228
4th	5.7	196 —198	1.5135	1.0251	45.15	230
Residue and loss	2.0					
Isopropylchlorobenzene						
ortho [6]		191.08	1.5167	1.0341		
meta [6]		198.3	1.5117	1.0208		
para [6]		195 —197 (730mm)	n_D^{25} 1.5140	d_{20}^{20} 1.0022		

• Calculated for $C_9H_{11}Cl$, MR_D 45.03.

TABLE 4

Fractions and butylchlorobenzenes	Amount of fraction (wt. %)	Boiling point at 760 mm	n_D^{20}	d_4^{20}	MR_D^*	Melting point of oxidation products
1st	4.8	210.0—212.0°	1.5122	—	—	—
2d	54.2	212.0—214.0	1.5109	1.0130	49.84	201°
3rd	32.0	214.0—216.5	1.5105	1.0090	49.95	236
4th	4.9	216.5—218.0	1.5105	—	—	238
Residue and loss	3.0					
p-tert-butylchlorobenzene [7]	—	210 —212 (730mm)	1.5121	d_{20}^{20}1.0035		
p-sec-butylchlorobenzene [7]	—	212 —214 (730mm)	n_D^{15} 1.4995	d_{20}^{20}1.0010		
p-n-butylchlorobenzene [8]	—	225 —228	—	—		

• Calculated for $C_{10}H_{13}Cl$, MR_D 49.65.

SUMMARY

1. The alkylation of chlorobenzene with ethyl, n-propyl, and n-butyl bromides in the presence of metallic aluminum has been carried out.

2. It has been shown that the yields of alkylchlorobenzenes (based on the para-isomers) increase with increasing molecular weights of the alkyl bromides. Under optimum conditions the yields, based on the alkyl bromides used, are: ethylchlorobenzene 46%, isopropylchlorobenzene 59%, and butylchlorobenzenes 69%.

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ISOMERIZATION OF POLYMETHYLENE HYDROCARBONS BY THE ACTION OF ALUMINUM CHLORIDE

XXI. ISOMERIZATION OF CYCLOHEXYLCYCLOPENTANE

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E. G. Treshcheva

In previous work one of us has shown [1] that dicyclopentyl in the presence of aluminum chloride is practically completely isomerized to the condensed system trans-decahydronaphthalene. When the hydrocarbon is placed in contact with aluminum chloride at 20°, the reaction starts instantaneously and proceeds with the evolution of much heat. Cyclohexylcyclopentane undergoes an analogous isomerization in contact with aluminum chloride, approximately 90% of it being converted into trans-methyldecahydronaphthalene. The presence of the latter compound in the reaction products was demonstrated by means of catalytic dehydrogenation and was confirmed by spectral analysis. The isomerization of cyclohexylcyclopentane, when it is contacted with aluminum chloride at 25°, actually proceeds at 100° because of the heat given off in the reaction, and it is complete in a few minutes. If the reaction mixture is heated for a long time at 100°, the composition of the products is changed somewhat because of the appearance of a small amount of products of further isomerization and cracking. When the reaction is carried out at 0°, the course of the isomerization of cyclohexylcyclopentane is the same as described above, but the extent of the reaction is less.

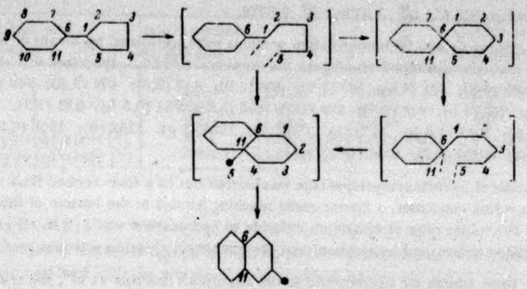
The transition from the bicyclic systems of dicyclopentyl and cyclohexylcyclopentane to the condensed bicyclic systems of decahydronaphthalene and beta-methyldecahydronaphthalene under our experimental conditions is evidently an irreversible process, since up to now there has been no indication of a transition of decahydronaphthalene or its homologs to the isomeric uncondensed cyclic systems.

The mechanism of the isomerization of cyclohexylcyclopentane may be represented by one of the following schemes.

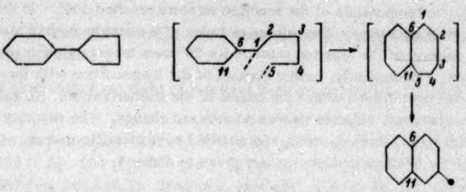
According to Schemes (I) and (II) expansion of the five-membered ring must first occur, and the formation of new carbon-carbon bonds – according to the first scheme between carbon atoms 5 and 6 with the formation of spiroundecane, and according to the second scheme between carbon atoms 5 and 11 with the formation of the condensed system from a six-membered and a seven-membered ring. Scheme (III) assumes the formation of methylcyclopentylcyclopentane as an intermediate product. The process in question must in any case terminate in the isomerization of the intermediate products to methyldecahydronaphthalene. The formation of spiroundecane (Scheme I) does not explain the vigor of the reaction, since contact of spiroundecane with aluminum chloride, as shown by one of us [2], is not attended by evolution of heat, and isomerization of the hydrocarbon is appreciable only when the reaction mixture is heated, starting around 50°.

Formation of the condensed hydrocarbon according to Scheme (II) is not very likely, since up to now the possibility of isomerization of hydrocarbons of the cyclopentane and cyclohexane series with expansion of the rings to seven members has not been demonstrated. Scheme (III) most probably represents the isomerization of cyclohexylcyclopentane.

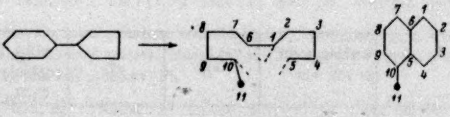
(I)



(II)



(III)



Now well known is the ability of cyclohexane to isomerize under the influence of aluminum chloride with contraction of the ring to methylcyclopentane, and in our case to methylcyclopentylcyclopentane, which by analogy with dicyclopentyl [1] must isomerize to methyldecahydronaphthalene. However, the true mechanism of such conversions can be finally established only by careful study of the kinetics of the isomerization of various cyclic hydrocarbons, using exact physicochemical methods of investigation.

EXPERIMENTAL

Cyclohexylcyclopentane was prepared from phenylmagnesium bromide and cyclopentanone.

Phenylcyclopentanol, prepared from cyclopentanone and phenylmagnesium bromide, distilled at 121-122° (10 mm) and had the following constants:

n_D^{15} 1.5459, d_4^{15} 1.0614, MR_D 48.34; calc. 48.72.

N. D. Zelinsky [3] gives for phenylcyclopentanol-1 b.p. 132-133° (18 mm), n_D^{19} 1.5472, d_4^{19} 1.0609, MR_D 48.43.

Phenylcyclopentene was prepared by the dehydration of the carbinol with iodine and had the following constants:

b.p. 228-229° (752 mm), m.p. 23°, n_D^{25} 1.5712, d_4^{25} 0.9870; MR_D 46.95; calc. 47.03.

Cyclohexylcyclopentane was prepared by hydrogenation of phenylcyclopentene over platinized carbon at 200-205°. Traces of phenylcyclopentene were removed by chromatographing, after which the cyclohexylcyclopentane was distilled in vacuo over metallic sodium and had the following constants:

b.p. 96-98° at 22 mm (215-217° at 758 mm), n_D^{20} 1.4722, d_4^{20} 0.8750, MR_D 48.65; calc. 48.60.

Evans [4] gives b.p. 215.5°, n_D^{20} 1.4728, d_4^{20} 0.8758.

Cyclohexylcyclopentane and its isomerization products were examined by means of their Raman spectra. The intensity of the lines was estimated visually on the usual scale of 10. Spectrum of cyclohexylcyclopentane: 230 (0.3); 284 (5); 303 (0.6); 326 (0.5); 383 (1.5); 406 (0.6); 437 (2.5); 474 (1.8); 509 (0.3); 587 (0); 732 (0.1); 769 (0.3); 790 (4 b); 846 (0.8); 870 (1.5); 895 (3.5); 951 (0.5 b); 978 (1.3); 1036 (8); 1040 (1.5); 1085 (2.5); 1091 (1.5); 1158 (1.5 b); 1175 (1); 1187 (1); 1227 (1 g); 1262 (5); 1304 (0.3); 1312 (0.5); 1337(1) 1346 (1.5); 1366 (0.2); 1382 (0.2); 1443 (10).

The isomerization of cyclohexylcyclopentane was carried out in a four-necked flask equipped with a mechanical stirrer, a reflux condenser, a thermometer reaching almost to the bottom of the flask, and a syringe for taking samples. The molar ratio of aluminum chloride to hydrocarbon was 1 : 3 in all experiments. The hydrocarbon was distilled before each experiment and the aluminum chloride was sublimed.

Experiment I. Upon adding the hydrocarbon to the aluminum chloride at 25°, the reaction began instantaneously. After 10 minutes the temperature of the reaction mixture reached 100°. It then began to drop and in 40-45 minutes was at room temperature. The refractive index of a suitably washed sample changed from n_D^{20} 1.4722 to n_D^{20} 1.4660. Stirring of the reaction mixture for 20 hours longer at room temperature had no effect on the refractive index. Consequently, further contact of the hydrocarbon with the aluminum chloride after the vigorous reaction was over did not affect the course of the isomerization. No gaseous products were evolved in the reaction; the aluminum chloride showed no outward change. The reaction product, obtained in 80% yield, was separated with water, washed, dried, and distilled over metallic sodium. Constants for the fractions from the distillation of the beta-methyldecalins are given in Table 1.

TABLE 1

Fraction Nos. and hydrocarbons	Boiling point at 752 mm	n_D^{20}	d_4^{20}	MR_D found (calculated for $C_{11}H_{20}$ 48.60)
Cyclohexylcyclopentane	215 —217°	1.4722	0.8750	48.65
1st fraction (6.5%)	196 —199.5	1.4639	0.8584	48.84
2d fraction (19.5%)	199.5—201.5	1.4665	0.8615	48.90
3rd fraction (47.0%)	201.5—202.5	1.4672	0.8634	48.85
4th fraction (20.5%)	202.5—205	1.4689	0.8667	48.82
trans-β-Methyldecalin [5]	76 (12mm)	1.4698	0.8693	48.85
trans-β-Methyldecalin [6]	76 (12mm)	1.4681	0.8670	48.75
cis-β-Methyldecalin [5]	84 (12mm)	1.4751	0.8846	48.47

From the data presented it is apparent that the constants for the 2d, 3rd, and 4th fractions are rather close to one another and to the constants for trans-β-methyldecahydronaphthalene. At the same time they differ significantly from the constants for cis-β-methyldecahydronaphthalene.

1st fraction. Found %: C 86.72; H 13.27.

4th fraction. Found %: C 86.70; H 13.48. $C_{11}H_{20}$. Calculated %: C 86.80; H 13.15.

From the analytical data for the end fractions and the constants for the 2d-4th fractions it follows that the mixture of hydrocarbons obtained from the reaction of aluminum chloride with cyclohexylcyclopentane is the product of isomerization, possibly with the starting hydrocarbon as an impurity. In the first fraction the presence of products of further isomerization may be suggested. The 2d-4th fractions • were dehydrogenated over 20% platinized carbon at 300-305° in a weak stream of carbon dioxide. The products of catalysis, carried out to a constant refractive index, agreed closely in their constants with β-methylnaphthalene (Table 2). The picrates

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• 1st fraction was not treated because of a small amount of dehydrogenation.

TABLE 2

Fraction Nos. and hydrocarbons	Boiling point at 750 mm	n_D^{20}	d_4^{20}	Melting point of picrates
2	240.5°	1.6024	0.9969	115.5—116°
3	238.0	1.6040	0.9985	115
4	237.0	1.6002	0.9920	114
β-Methylnaphthalene [7]	241.1	1.60192 (40°)	0.99045 (40°)	115 —116 [8]
α-Methylnaphthalene [7]	244.8	1.61494 (25°)	1.0163 (25°)	141 —142 [8]

obtained from the products of catalysis agreed in melting point with the picrate of β-methylnaphthalene. A mixture of the picrate obtained with the picrate of β-methylnaphthalene melted at 115.5-116°, i. e. there was no depression.

Thus it was shown by means of catalytic dehydrogenation that methyldecalin is the product of the isomerization of cyclohexylcyclopentane.

To confirm this observation, portions of fractions 2-4 (before dehydrogenation) were subjected to spectral analysis.

The spectra were very similar: 238 (1); 257 (1 b); 327 (1 g); 352 (1.5); 373 (12); 410 (4); 439 (2.5), 462 (2.5); 500 (4); 533 (1.5); 594 (1); 753 (12); 767 (1.5); 792 (1); 837 (1.5); 851 (5); 863 (1.3); 889 (1); 920 (1); 956 (1 g); 987 (1); 1015 (1.5); 1043 (8); 1056 (2); 1080 (3 b); 1144 (2 b); 1165 (10); 1202 (3); 1219 (0.5); 1241 (2); 1255 (4.5); 1267 (1.5); 1296 (1); 1346 (7); 1360 (8); 1443 (9); 1460 (10).

Trans-β-methyldecahydronaphthalene was obtained by hydrogenation of β-methylnaphthalene in the vapor phase over partially leached skeletal nickel [9] at 210° and had constants close to those reported for the same hydrocarbon by Levina and Kulikov [5]:

b.p. 202° at 760 mm, n_D^{20} 1.4694, d_4^{20} 0.8710, MR_D 48.64; calc. 48.60.

Spectrum of trans-β-methyldecahydronaphthalene: 240 (0); 276 (0); 329 (0.8); 353 (0.5); 373 (4.5); 409 (2 b); 444 (0); 464 (0.2); 500 (4); 530 (0.1); 593 (2); 621 (0.4); 735 (1); 755 (12); 796 (0.3); 849 (4.5); 863 (0); 929 (0); 978 (0); 1015 (1); 1042 (5.5 b); 1056 (1); 1076 (3.5); 1142 (0.1 g); 1165 (6); 1197 (1.5 b); 1241 (3 g); 1267 (2 g); 1296 (0.4); 1347 (2.5); 1354 (3); 1440-1460 (10 g).

Comparison of the Raman spectrum obtained by us for the isomerization product of cyclohexylcyclopentane with the spectrum of trans-β-methyldecalin shows that these spectra are basically identical. All the most intense lines of trans-β-methyldecalin also appear as the most intense lines in our spectrum. There is a slight difference in the weak lines of the spectra, which may perhaps be explained by a difference in the conditions of exposure (the substances were exposed in different instruments).

Experiment II was carried out at 100°. The reaction mixture, after the vigorous reaction was over, was heated for an additional 20 hours on a boiling water bath. The reaction product was washed, dried, and distilled over metallic sodium:

1st fraction up to 190° (5.9%), n_D^{20} 1.4420, d_4^{20} 0.7703; 2d fraction 190-199° (29.4%), n_D^{20} 1.4644, d_4^{20} 0.8530; 3rd fraction 199-201° (54.1%), n_D^{20} 1.4670, d_4^{20} 0.8605.

From the distillation data it appears that the reaction at 100° follows the same course as in the preceding experiment. However, because of the comparatively high temperature and the duration of the experiment, lower boiling fractions (the 1st and part of the 2d) appeared, possibly containing cracking products.

The spectra of the 2d and especially the 3rd fraction were very similar to the spectra obtained in the preceding experiment. From this it can be concluded that the isomerization products of the two experiments were similar in composition.

Spectrum of isomerization products: 239 (0.4); 276 (0.1); 325 (0.3); 345 (1); 373 (5.5); 397 (0); 406 (3); 441 (1.6); 465 (1.5); 494 (1); 501 (3.5); 529 (0.5); 556 (0.4); 592 (0.5); 651 (0.2); 695 (0.3); 753 (10); 769 (2); 792 (0.1); 838 (1); 853 (3); 867 (0.5); 893 (0.6); 912 (0.4); 954 (0.4); 963 (0.1); 987(0.5); 1015 (0.5); 1040 (7); 1056 (2); 1080 (1.5 g); 1102 (0.3); 1144 (0.8); 1167 (7); 1202 (3); 1218 (0.3); 1241 (1 db); 1255 (5); 1267 (1); 1346 (6); 1360 (8); 1443 (9); 1460 (10).

Experiment III was carried out at 0°. The hydrocarbon, previously cooled to 0°, was mixed at this temperature with the aluminum chloride. The mixture of the components, in the same ratio as in the preceding experiments, was stirred continuously for 6 hours at 0°. The refractive index of the washed and dried reaction product changed insignificantly from n_D^{20} 1.4722 to n_D^{20} 1.4705. The change in the Raman spectrum also was insignificant:

284 (7); 306 (0.3); 322 (0.5); 327 (1); 343 (0.2); 373 (2); 385 (2); 409 (1.5); 439 (2.5); 472 (1); 477 (2); 501 (2); 530 (0.3); 587 (0.3); 681 (0.2); 753 (3); 785 (5); 795 (5); 850 (2); 868 (2.5); 895 (4.5); 922 (0.4); 926 (0.4); 976 (3); 1033 (9); 1045 (5); 1085 (5); 1091 (4); 1165 (3); 1178 (3); 1190 (3); 1200 (2); 1226 (0.2); 1263 (8); 1296 (0.4); 1313 (1.5); 1337 (1.5); 1346 (2); 1364 (0.3); 1382 (0.3); 1442 (10).

Comparison of the spectrum of the reaction product of this experiment with the spectra of cyclohexylcyclopentane and trans-β-methyldecalin indicated that along with unreacted starting hydrocarbon (lines at 284, 439, 785-795, 895, 1033) a certain amount of trans-β-methyldecalin was present in the products.

SUMMARY

1. The isomerization of cyclohexylcyclopentane through the action of aluminum chloride has been investigated.

2. It has been shown that within the temperature range from 0 to 100° trans-β-methyldecalin is the isomerization product.

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THE REACTION OF SILICON TETRACHLORIDE WITH ACETIC AND BENZOIC ANHYDRIDES

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In 1868 the preparation of silicon tetraacetate by heating a mixture of acetic acid and acetic anhydride with silicon tetrachloride was described [1]. This same compound was obtained by heating silicon tetrachloride and sodium acetate in an inert solvent [2]. Silicon tetraacetate also was prepared by heating an ether solution of acetic acid and silicon tetrachloride [3]. The latter two reactions give a low yield – 50 and 30% respectively – and not a very pure product (containing silicon dioxide and chlorine), since heating causes decomposition of silicon tetraacetate [1].

By the reaction of silicon tetrachloride with the appropriate acids [4-6] other mixed anhydrides were obtained: silicon tetraformate, tetrabutyrate, and tetrabenzoate, which have been employed for a series of interesting syntheses.

We have found that mixed anhydrides of silicic acid are obtained in several instances by direct reaction of silicon tetrachloride with acid anhydrides. The reaction takes place under less severe conditions than in the cases reported above and results in the formation of purer products in better yield.

When silicon tetrachloride was mixed with acetic anhydride in a 1 : 4 molar ratio (10 g of $SiCl_4$ to 24 g of acetic anhydride), a negligible amount of heat was evolved and in 10-15 minutes rather large crystals of silicon tetraacetate settled out. These were separated on a glass filter equipped with a cover with a calcium chloride tube, and were dried in a vacuum desiccator. M.p. 110°. Yield about 80%. After the acetyl chloride had been distilled out of the filtrate from the silicon tetraacetate crystals, it was possible to obtain a further quantity of the latter.

The silicon tetraacetate obtained in this way was usually very pure. If necessary, it could be recrystallized from acetic anhydride.

Silicon tetraacetate also was formed when other proportions of silicon tetrachloride and acetic anhydride were used, but crystals of it did not precipitate unless there was sufficient acetic anhydride to equal the 1 : 4 ratio.

Found %: Si 10.3, 10.5; CH_3COO^- 89.5, 89.2. $(CH_3COO)_4Si$. Calculated %: Si 10.6; CH_3COO^- 89.4.

Silicon tetrabenzoate was prepared by refluxing a mixture of silicon tetrachloride and benzoic anhydride in a 1 : 4 molar ratio (10 g of $SiCl_4$ to 54 g of benzoic anhydride) on a boiling water bath for one hour. After the reaction was over, the benzoyl chloride formed was distilled off by heating carefully (preferably in vacuo) and the silicon tetrabenzoate remained in the flask as a very viscous, yellow mass. The yield was nearly theoretical. The silicon tetrabenzoate obtained in this way started to crystallize after standing for a long time.

Found %: Si 5.5 $(C_6H_5COO)_4Si$. Calculated %: Si 5.47.

Upon distillation even in vacuo (5 mm) silicon tetrabenzoate decomposed with the formation of benzoic anhydride.

SUMMARY

It has been established that silicon tetrachloride can react directly with the anhydrides of organic acids to form mixed anhydrides of the organic acid and orthosilicic acid. This reaction takes place under less severe conditions than the reaction of silicon tetrachloride with the corresponding acids. By means of this reaction, silicon tetraacetate and silicon tetrabenzoate have been obtained in good yield.

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SYNTHESIS OF HOMOLOGS OF 1,11-UNDECINOIC ACID

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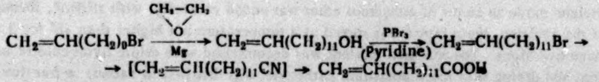
It is known that some acids with double bonds exert an inactivating effect on the virus group. It seemed to be of interest also to investigate acids with a triple bond in this respect. In this connection we have described the preparation of 1,12-do-, 1,13-tri-, and 1,14-tetradecinoic acids from the corresponding acids with a double bond by the addition of bromine and subsequent dehydrobromination. The 1,12-do- and the 1,13-tridecenoic acids were obtained by a method previously described [1]. 1,14-Tetradecenoic acid was prepared according to the following scheme:



$$CH_2{=}CH(CH_2)_9Br \xrightarrow[Mg]{\overset{CH_2-CH_2}{\diagdown O \diagup}} CH_2{=}CH(CH_2)_{11}OH \xrightarrow[(Pyridine)]{PBr_3} CH_2{=}CH(CH_2)_{11}Br \rightarrow$$

$$\rightarrow [CH_2{=}CH(CH_2)_{11}CN] \rightarrow CH_2{=}CH(CH_2)_{11}COOH$$

In the literature there is described [2] the preparation of 1,13-tridecenol by the reduction of an ester of tridecenoic acid, obtained from undecenyl bromide by a series of steps. We have obtained 1,13-tridecenol by a much simpler method – the action of ethylene oxide on the organomagnesium compound from 1,11-undecenyl bromide. In preparing 1,13-tridecenyl bromide from the corresponding alcohol and hydrogen bromide [2], a side reaction occurs – the addition of HBr to the double bond, which leads to the formation of a mixture of substances difficult to separate; we therefore prepared the bromide by the reaction of phosphorus tribromide and the tridecenol in the presence of pyridine. The nitrile of the tetradecenoic acid was prepared in the usual way and subjected to saponification without purifying. The addition of bromine to the double bond of the olefinic acids was carried out in carbon bisulfide at a low temperature; after removal of the solvent, the dibromoacids were dehydrobrominated without prior purification by heating with an alcoholic solution of potassium hydroxide (1 : 10). The alkinecarboxylic acids obtained were colorless, crystalline substances, easily soluble in the common organic solvents and crystallizing from small amounts of petroleum ether (b.p. 80-90°). The homologs of undecinoic acid were characterized by their p-bromophenacyl esters. The ethinyl group was determined by a method based on titration of the nitric acid freed by the action of $AgNO_3$ on the acetylenic compound [3].

The alkinecarboxylic acids prepared exerted a bacteriostatic action on acid-resisting bacteria and a fungistatic action on pathogenic fungi.* These acids were not active against the virus group, while the corresponding acids with a double bond, and also 1,11-undecylenic and 1,11-undecinoic acids had a virus-neutralizing effect in experiments in vitro.**

EXPERIMENTAL

1,12-Dodecinoic acid. A solution of 8 g of bromine in 15 ml of carbon bisulfide was added gradually, with stirring, to a solution of 9.9 g of 1,12-dodecenoic acid in 20 ml of carbon bisulfide maintained at a temperature no higher than +10°. After the addition was completed, the mixture was stirred at the same temperature for another 30 minutes. The carbon bisulfide was then removed in vacuo, and the dibromododecanoic acid obtained was added to a solution of 17.9 g of chemically pure KOH in 180 ml of ethyl alcohol and refluxed for

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* Experiment carried out by S. N. Milovanova.

** Experiment carried out by N. S. Bogdanova.

3.5 hours. The alcohol was distilled off in vacuo and the residue was dissolved in water and made acid to congo by adding hydrochloric acid (1 : 1). After the usual treatment, the product was distilled in vacuo; b.p. 182-192° (15 mm); the material partially crystallized upon cooling. The crystals were centrifuged out and recrystallized several times from petroleum ether, m.p. 43.5-44.5°.

Found %: C 73.04, 73.07; H 10.30, 10.15; $HC\equiv C$ 12.58. $C_{12}H_{20}O_2$. Calculated %: C 73.42; H 10.27; $HC\equiv C$ 12.75.

p-Bromophenacyl ester with m.p. 67°.

Found %: Br 20.57. $C_{20}H_{25}O_3Br$. Calculated %: Br 20.32.

1,13-Tridecinoic acid. This compound was obtained in a manner analogous to the 1,12-dodecinoic acid. M.p. 57.5°.

Found %: C 74.51, 74.17; H 10.21, 10.47; $HC\equiv C$ 11.83. $C_{13}H_{22}O_2$. Calculated %: C 74.24; H 10.54; $HC\equiv C$ 11.90.

p-Bromophenacyl ester m.p. 78°.

Found %: Br 19.65. $C_{21}H_{27}O_3Br$. Calculated %: Br 19.62.

1,13-Tridecenol. The organomagnesium compound was prepared in the usual way from 2.1 g of magnesium and 20 g of 1,11-undecenyl bromide. The flask was then equipped with a thermometer, the condenser was replaced by a coil cooled with ice, the flask was immersed in a cooling mixture, and a solution of 19 g of technical ethylene oxide in 55 ml of anhydrous ether was added carefully, with stirring, through a dropping funnel. At the end of the addition, the mixture was stirred at a temperature not higher than +5° for 3.5 hours and then allowed to stand overnight. The reaction mixture was decomposed with dilute hydrochloric acid and after the usual treatment and drying with fused potassium carbonate, was distilled in vacuo; a fraction was collected boiling 146-154° (9.5 mm). Yield 60%. The 1,13-tridecenol obtained was used without further purification for the preparation of 1,13-tridecenyl bromide.

1,13-Tridecenyl bromide. A solution of 28.1 g of tridecenol and 0.8 g of pyridine in 80 ml of anhydrous ether was placed in a three-necked flask fitted with a stirrer and a reflux condenser; to this was added gradually, with stirring, 13.5 g of phosphorus tribromide, maintaining continuous boiling. After the addition was completed, the mixture was boiled for 2 hours and allowed to stand over-night. After the usual treatment, the product was distilled twice in vacuo. B.p. 143.5-145° (8.5 mm). Yield 50%.

1,14-Tetradecenoic acid. Seven grams of 95% KCN was dissolved in 10 ml of warm water, 17.5 g of tridecenyl bromide and 70 ml of alcohol were added, and the mixture was refluxed, with stirring, for 24 hours. Then 14.5 g of powdered KOH was added and the mixture was boiled with stirring for 30 hours, cooled, poured into 45 ml of 20% hydrochloric acid, and extracted with ether. After the usual treatment, the product was distilled in vacuo. B.p. 143.5-144.5° (1 mm). Yield 11.1 g (75%). Colorless, crystalline substance, easily soluble in common organic solvents. After recrystallization from petroleum ether, m.p. 35.5°.

Found %: C 74.27, 74.06; H 11.35, 11.61 $C_{14}H_{26}O_2$. Calculated %: C 74.28; H 11.57.

1,14-Tetradecinoic acid. This compound was prepared in a manner analogous to 1,12-dodecinoic acid. After several recrystallizations from a mixture of petroleum ether (b.p. 80-90°) and a small amount of acetone, it melted at 56.5-57.5°.

Found %: C 74.71; H 10.79; $HC\equiv C$ 11.10. $C_{14}H_{24}O_2$. Calculated %: C 74.95; H 10.78; $HC\equiv C$ 11.16.

p-Bromophenacyl ester m.p. 73-74°.

Found %: Br 19.12. $C_{22}H_{29}O_3Br$. Calculated %: Br 18.99.

SUMMARY

For the purpose of studying their biological action, 1,14-tetradecenoic acid and 1,12-do-, 1,13-tri-, and 1,14-tetradecinoic acids were prepared and characterized.

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INFLUENCE OF THE NATURE OF THE ALCOHOLIC COMPONENT ON THE VELOCITY OF ALKALINE HYDROLYSIS OF ESTERS

II. HYDROLYSIS OF ESTERS OF PHENOL AND BENZYL ALCOHOL

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The influence of structural characteristics of the acid and alcohol on the kinetics of esterification and hydrolysis of esters was studied in the classic work of N. A. Menshutkin [1]. A number of authors later studied the kinetics of hydrolysis of esters – mainly esters of aliphatic alcohols with aliphatic and aromatic carboxylic acids [2-4]. Investigations were made of the influence of the nature of the alcohol [6, 7] and of the acid [5, 8, 14, 15] on the velocity of hydrolysis, of the influence of temperature, solvents, catalysts, etc. Much less attention has been paid to esters of phenol and benzyl alcohol with aliphatic acids [9-11]. In esters of phenol both components possess acidic characteristics; it was therefore of interest to establish their effect upon the stability of the ester bond in comparison with corresponding esters of ethyl and benzyl alcohols.

In the investigation of the hydrolysis of esters of acetic and benzoic acids with various alcoholic components, it was established that intensification of the acidic properties of the alcohols increases the rate of hydrolysis [12]. This phenomenon was confirmed by Hinshelwood [13] in studies of the rate of hydrolysis of substituted esters of phenol and benzoic acid.

We were interested in studying this effect with esters of phenols and aliphatic acids, and at the same time in clarifying the effect of the distance of the benzene ring from the carbon of the carboxyl (both in the alcoholic and in the acidic component) on the rate of hydrolysis of esters.

EXPERIMENTAL

The rate of hydrolysis was studied with esters of phenol and benzyl alcohol with acetic, propionic, butyric, valeric, isobutyric, isovaleric, benzoic, phenylacetic and phenylpropionic acids; also with esters of phenylethyl alcohol with butyric and benzoic acids. We prepared all of these esters and checked their purity by determinations of boiling point, specific gravity and refractive index. Saponification of the esters was effected with potassium hydroxide in a 70% aqueous dioxane medium. Our solvent ensured adequate reaction velocity, homogeneity of the medium and absence of secondary reactions. The reaction velocity was determined by back-titration of the excess of acid in presence of cresol red as indicator. Due to their relatively high rate of hydrolysis, the esters were saponified at temperatures of 0 and 15°. The molar concentrations of ester and alkali were so selected that their ratio was roughly 1:3. The weights of esters were checked from the total consumption of alkali for saponification. Fuller details of the experimental procedure are given in the preceding communication [12].

The velocity constants of hydrolysis were calculated from the equation for a bimolecular reaction. A double consumption of alkali was assumed for esters of phenol and the velocity constants were calculated from the equation

$$\frac{dx}{dt} = k\,(a-2x)\,(b-x).$$

The exponential factor log Pz and the activation energy E were calculated from the Arrhenius equation. Results are presented in Table 1. Dimensions of terms: K - liters · mole^{-1} · sec.$^{-1}$; log Pz - liters · mole^{-1} · sec.$^{-1}$; E - cal/mole.

TABLE 1

Influence of Nature of Acid on Velocity of Hydrolysis of Esters of Phenol, Benzyl Alcohol and Phenylethyl Alcohol

Acid	Esters of phenol				Esters of benzyl alcohol			
	$K_0 \cdot 10^3$	$K_{15} \cdot 10^3$	$\log Pz$	E	$K_0 \cdot 10^3$	$K_{15} \cdot 10^3$	$\log Pz$	E
Acetic	63.37	245.4	10.09	14100	10.19	35.50	8.41	13000
Propionic	38.57	150.0	9.92	14150	5.04	17.87	8.26	13200
Butyric	22.75	91.0	9.92	14440	2.79	10.16	8.25	13500
Valeric	14.68	59.8	9.88	14630	1.50	5.54	8.07	13620
Isobutyric	17.50	74.88	10.33	15100	1.75	7.16	9.05	14750
Isovaleric	5.84	24.47	9.69	14900	0.67	2.57	8.07	14050
Benzoic	5.000	22.30	10.19	15600	0.60	2.46	8.49	14630
Phenylacetic	177.40	605.00	9.48	12780	16.59	53.70	8.01	12230
Phenylpropionic	48.23	165.00	8.96	12830	5.68	18.60	7.63	12350
	Esters of phenylethyl alcohol							
Butyric	2.45	8.70	7.95	13190				
Benzoic	0.39	1.57	8.11	14390				

DISCUSSION OF RESULTS

The results show that the strength of the ester bond in esters of carboxylic acids depends upon all the changes taking place in composition and structure of the molecule. Increase in length of the alkyl radical when passing from acetic to valeric acid in esters of phenol and benzyl alcohol leads to a fall in the rate of hydrolysis, which is associated with an increase in activation energy. In this series of experiments the exponential factor exhibits a very slight but falling trend. In this case, therefore, the change of velocity constant depends solely upon the change of activation energy. This behavior is consistent with the general rule (on the basis of numerous examples) that substitution remote from the reaction center only affects the velocity to the extent that the activation energy changes, while the factor Pz remains constant [16].

TABLE 2

Influence of Acid Strength on Rate of Hydrolysis of Esters

R in $RCOOC_6H_5$	Velocity constants of hydrolysis $K_{15} \cdot 10^3$	Dissociation constants of acids [17] $K_{25} \cdot 10^6$
H	Saponified rapidly	214.2
CH_3	245.4	18.0
C_2H_5	150.0	13.4
C_6H_5	22.3	63.0
$C_6H_5CH_2$	605.0	55.6
$C_6H_5CH_2CH_2$ . .	165.0	22.7

The presence of side chains in the acid radical (transition from butyric to isobutyric acid and from valeric to isovaleric acid in esters of phenol and benzoic acid) considerably reduces the velocity of hydrolysis due to an appreciable increase in activation energy. The observed changes in the magnitudes of the velocity constants of hydrolysis depend not only on the size of the alkyl radical and its isomerism but also on the acidic component (Table 2).

Increase in strength of the acid forming the ester reduces the strength of its ester bond. This generalization is fully confirmed by our data for the hydrolysis of esters of phenol and benzyl alcohol. In the case of benzoic acid there is a slight inconsistency between acid strength and rate of hydrolysis. Irrespective of the nature of the alcohol, esters of benzoic acid are saponified more slowly than the corresponding esters of acetic acid (Table 3). The sharp drop in rate of hydrolysis is due to a considerable rise in activation energy on passing from acetic to benzoic acid.

The phenyl radical, constituting a system of conjugated σ- and π-bonds and having an electron-accepting character, is bound to weaken the C-O bond, i. e. is bound to favor hydrolysis. Esters of benzoic acid, however, are saponified more slowly than esters of aliphatic acids. This behavior is evidently associated with the steric influence of the phenyl group which is in the vicinity of the carboxylic carbon. While the inductive effect of the phenyl radical is favorable to hydrolysis (as exemplified by phenylacetic and phenylpropionic acids), in esters of benzoic acid there is the additional steric effect which acts in the opposite direction. The spatial effect of the phenyl radical must therefore be taken into account in addition to the electron-accepting action [18]. In the case of esters of substituted benzoic acid we observe an exact parallelism between the dissociation constants of the acids and the reactivity of the ester bond [19, 20].

TABLE 3

Hydrolysis of Esters of Acetic and Benzoic Acids with Various Alcoholic Components

Alcoholic components	Acid components					
	Acetic acid			Benzoic acid		
	$K_{18} \cdot 10^{9}$	$\log P_z$	E	$K_{18} \cdot 10^{9}$	$\log P_z$	E
Ethyl alcohol	13.2	9.09	14450	1.47	8.88	15430
Benzyl alcohol	35.5	8.41	13000	2.46	8.48	14630
Phenylethyl alcohol	—	—	—	1.57	8.11	14390
Phenol	245.4	10.09	14100	22.3	10.19	15600
1,4'-Dihydroxydiphenylsulfone•	796.0	9.14	12180	121.50	9.28	13440
4-Hydroxydiphenylsulfone	1324.0	9.04	11750	225.3	9.14	12900

• These alcohols can be regarded as phenol substituted by the electronegative groups: $C_6H_5SO_2$ (in the case of hydroxydiphenylsulfone) and $HOC_6H_4SO_2$ (in the case of partial ethers of dihydroxydiphenylsulfone [23].

We studied the influence of the nature of the alcoholic radical with reference to esters of phenol, benzyl alcohol and two esters of phenylethyl alcohol. In respect of rate of hydrolysis these alcohols can be arranged in the order:

$$C_6H_5CH_2CH_2OH < C_6H_5CH_2OH < C_6H_5OH.$$

In conjunction with the results of the preceding work [12] we obtain the following more complete series:

$$C_2H_5OH < C_6H_5CH_2CH_2OH < C_6H_5CH_2OH < C_6H_5OH < HOC_6H_4SO_2C_6H_4ONa <$$
$$< HOC_6H_4SO_2C_6H_5.$$

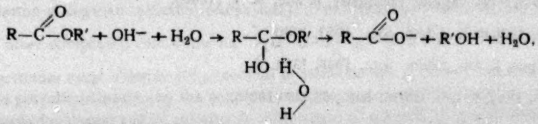
Introduction of a phenyl radical into the alcoholic component increases the rate of hydrolysis. This increase is the more marked the nearer the phenyl radical is to the carbon of the carboxyl group.

The influence of the distance of the phenyl radical from the carboxyl carbon upon the rate of hydrolysis may be quantitatively characterized by calculation of the transfer of influence. Comparing the rate of hydrolysis of esters of benzoic acids with various alcoholic components containing the phenyl radical, e.g. $C_6H_5COOC_6H_5$ (k_1), $C_6H_5COOCH_2C_6H_5$ (k_2), $C_6H_5COOCH_2CH_2C_6H_5$ (k_3), with the rate of hydrolysis of ethyl benzoate (k_4), the differences in their rates of hydrolysis appear to be due, firstly, to replacement of the alkyl radical by aryl, and, secondly, to the distance of the phenyl radical from the active reaction center. The difference in rates of hydrolysis of the ethyl and phenyl esters of benzoic acids can be related to the electronic influence of the phenyl radical (the electronic influence of the C_2H_5 radical can be neglected), and the ratio $k_1 : k_4 = 22.3 : 1.47 = 15$ can serve as a measure of the inductive influence of the phenyl radical upon the rate of hydrolysis. By carrying out similar calculations with benzyl alcohol and phenylethyl alcohol, we can determine the fall in inductive effect of the phenyl radical with increasing distance from the carboxyl carbon: $k_2 : k_4 = 2.46 : 1.47 = 1.67$. Separation of the benzene ring by one CH_2 group of the alcoholic component from the carboxyl carbon greatly weakens the influence of the phenyl radical on the rate of hydrolysis.

The effect of the phenyl radical can be similarly determined for esters of phenol with various acidic components containing the phenyl radical, e. g. $C_6H_5COOC_6H_5$ (k_1), $C_6H_5CH_2COOC_6H_5$ (k_2), and $C_6H_5CH_2CH_2COOC_6H_5$ (k_3), from the ratio of the velocity constants of hydrolysis of these esters to the velocity of hydrolysis of phenyl acetate (k_4): $k_1 : k_4 = 22.3 : 245.4 = 0.09$. In this case the ratio is less than unity due to the steric influence of the phenyl radical. For phenylacetic acid the factor expressing the inductive influence of the phenyl radical rises to 2.47 ($k_3 : k_1 = 605 : 245 = 2.47$), and this can serve as a measure of the inductive influence of the phenyl radical upon the electrophilicity of the carboxyl carbon when the benzene ring is separated from the latter by one CH_2 group. For esters of phenylpropionic acid the corresponding factor is 1.27.

Consequently, the introduction of a phenyl radical both into the acidic and the alcoholic component favors hydrolysis. In acids the favorable effect of the phenyl radical is manifested when the benzene ring is not directly bound to the carboxyl carbon. When a CH_2 group separates the phenyl from carboxyl, the influence of the phenyl upon the rate of hydrolysis is stronger if the phenyl is in the acidic component and not in the alcoholic component.

The experimental data are in harmony with the previously proposed mechanism of hydrolysis [12, 22, 23]. In alkaline hydrolysis of esters of carboxylic acids the mechanism of hydrolysis involves addition of OH^- ions to the carboxyl carbon and of a molecule of water to the alcoholic oxygen according to the scheme



$$R{-}\overset{O}{\overset{\|}{C}}{-}OR' + OH^- + H_2O \rightarrow R{-}\underset{HO}{\underset{|}{C}}{-}OR' \cdots H_2O \rightarrow R{-}\overset{O}{\overset{\|}{C}}{-}O^- + R'OH + H_2O,$$

followed by cleavage of the complex and loss of water [21]. A decisive factor in the hydrolysis of esters of carboxylic acids is the electrophilicity of the carboxyl carbon which depends both on the nature of the acidic and of the alcoholic component. The increase in the electrophilicity of the alcoholic and acidic radical due to the inductive effect must lead to an increase in the electrophilicity of the carboxyl carbon in the ester and thereby promote the addition of OH^- ions. Esters containing a phenyl radical both in the acidic and alcoholic component are therefore saponified with greater facility than esters containing solely alkyl radicals.

SUMMARY

The rate of alkaline hydrolysis of esters of phenol, benzyl alcohol, phenylethyl alcohol with aliphatic and aromatic carboxylic acids was investigated. It was established that esters of phenol are characterized by the highest velocity of hydrolysis. The closer the phenyl radical is to the carboxyl carbon, the greater is the influence of the phenyl radical upon the rate of hydrolysis. The introduction of the electronegative phenyl radical both into the acidic and the alcoholic component increases the rate of hydrolysis of the corresponding esters with the exception of esters of benzoic acid in which the phenyl radical is directly linked to the carboxyl carbon and its steric effect is superposed on the hydrolysis-promoting electronic effect.

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THE ALKYLATION OF CHLOROETHERS OF ORTHOSILICIC ACID AND METHYLETHOXYCHLOROSILANES

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N. P. Lobusevich

We know from the literature that the alkylation of tetraethoxysilane with organomagnesium compounds proceeds with facility in a medium of aromatic hydrocarbons, while the alkylation of silicon tetrachloride proceeds with difficulty under the same conditions. This is accounted for by the catalytic effect of tetraethoxysilane on the formation of organomagnesium compounds [1]. Definite interest is attached to the investigation of the behavior of other compounds containing the $>\!Si-O-C\!<$ grouping under the action of magnesium and alkyl halide, in particular ethyl chloride (in a medium of aromatic hydrocarbon). We have now studied the formation of liquid polyalkylsiloxanes by the action of magnesium and ethyl chloride on chloroethers of orthosilicic acid (ethoxychlorosilanes) and on substituted chloroethers of orthosilicic acid (methylethoxychlorosilanes). Chloroethers of orthosilicic acid were prepared by partial etherification of silicon tetrachloride with anhydrous ethanol in various ratios according to the scheme:

$$SiCl_4 + n\,C_2H_5OH \rightarrow Cl_{4-n}Si(OC_2H_5)_n + n\,HCl, \qquad (1)$$

where $n = 0.8$ to 2.0.

The resultant mixtures of chloroethers of orthosilicic acid are reacted with magnesium and ethyl chloride in toluene with initiation of the reaction by a small quantity (about 1%) of diethyl ether. As we had previously found [2], the organomagnesium compounds react in the first place with the chlorine atom linked to the silicon, and the reaction may be expressed by the equation:

$$Cl_{4-n}Si(OC_2H_5)_n + 2Mg + 2C_2H_5Cl \rightarrow (C_2H_5)_2SiCl_{2-n}(OC_2H_5)_n + 2MgCl_2. \qquad (2)$$

Hydrolysis of the reaction products with water gives a mixture of polyethylsiloxanes:

$$x\,(C_2H_5)_2SiCl_{2-n}(OC_2H_5)_n \xrightarrow{H_2O} [(C_2H_5)_2SiO]_x + x\,(2-n)\,HCl + nx\,C_2H_5OH. \qquad (3)$$

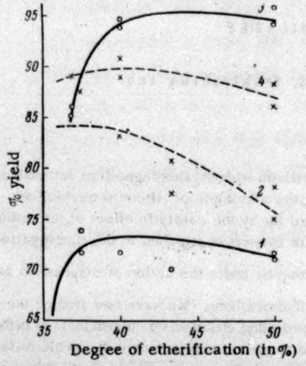
Ethylation and hydrolysis of the mixture of products of partial etherification of methyltrichlorosilane were similarly carried out:

$$CH_3SiCl_3 + n\,C_2H_5OH \rightarrow CH_3SiCl_{3-n}(OC_2H_5)_n + n\,HCl \qquad (4)$$

$$\begin{gathered} CH_3SiCl_{3-n}(OC_2H_5)_n + Mg + C_2H_5Cl \rightarrow \\ \rightarrow C_2H_5CH_3SiCl_{2-n}(OC_2H_5)_n + MgCl_2 \end{gathered} \qquad (5)$$

$$\begin{gathered} xC_2H_5CH_3SiCl_{2-n}(OC_2H_5)_n + xH_2O \rightarrow \\ \rightarrow [CH_3C_2H_5SiO]_x + x(2-n)HCl + nxC_2H_5OH. \end{gathered} \qquad (6)$$

Ethylation of the products of partial etherification of methyltrichlorosilane (5) proceeds satisfactorily when the reaction is initiated by ethyl iodide or diethyl ether. Results of experiments are plotted in the diagram. Here the abscissas are molar percentages of etherified atoms of chlorine ($\frac{n}{4} \cdot 100$ for $SiCl_4$ or $\frac{n}{3} \cdot 100$ for CH_3SiCl_3), and the ordinates are % yields of products. Curve 1 shows the yield of polydiethylsiloxanes referred to silicon tetrachloride [reactions (1) to (3)], curve 3 shows the yield of polymethylethylsiloxanes referred to methyltrichlorosilane [reactions (4) to (6)], curves 2 and 4 show respectively the yields of products of partial etherification according to reactions (1) and (4).



Ethylation of products of partial etherification of silicon tetrachloride and methyltrichlorosilane.
(See text for details).

The experimental data show that the yields of polyalkylsiloxanes, both from ethylation of the products of etherification of silicon tetrachloride and of methyltrichlorosilane, increase with increasing degree of etherification and reach a maximum for products with a degree of etherification of the order of 35-40%. When the degree of etherification of silicon tetrachloride is less than 35% and that of methyltrichlorosilane is less than 40%, the yields of polydialkylsiloxanes fall sharply, thereby reflecting an unsatisfactory course of the alkylation. The fall in yield cannot be due to the interaction of the organomagnesium compound because the chlorine linked to the silicon enters into this reaction more easily than the alkoxy group. It may therefore be assumed that when the degree of etherification of the chlorosilane is less than 35-40%, the formation of ethyl magnesium chloride from magnesium chloride in a hydrocarbon medium is slowed down.

EXPERIMENTAL

Partial etherification of silicon tetrachloride.

255 g of silicon tetrachloride was charged into a four-necked flask fitted with a reflux condenser connected to a hydrogen chloride absorber, a dropping funnel and a stirrer with seal. Dropwise addition (while stirring) was then made of 103.5 g of anhydrous ethyl alcohol in the course of 2-3 hours at 18-20°, after which the reaction mixture was heated for 2 hours with gradual rise of temperature to 115° in order to drive off the hydrogen chloride. 258.5 g of a mixture of chloroethers was obtained [93.6% of the theoretical amount on the basis of equation (1)].

Ethylation of products of partial etherification of silicon tetrachloride and hydrolysis of the mixture of products of ethylation. 44.5 g of magnesium turnings was charged into a flask fitted with a stirrer (with seal), a reflux condenser (connected to the atmosphere through a calcium chloride tube) and a thermometer. The flask was heated to 50°, after which a mixture of 3 ml ethyl chloride and 3 ml diethyl ether was added with stirring. The start of the reaction was marked by a sudden rise of temperature in the flask (to 70°). The flask was cooled in an ice bath, and after the temperature had fallen to 45-50° a mixture of 150 g of products of partial etherification of silicon tetrachloride, 136 g of ethyl chloride, 327 g toluene and 3 ml of diethyl ether was added at a steady rate over a period of 4-5 hours (temperature of 45-50° in the flask). Constant cooling of the flask in a water bath was necessary due to the exothermic character of the reaction during addition of the mixture. The reaction mass was afterwards gradually heated to 100° in the course of 2-3 hours, then cooled and subjected to hydrolysis. From the dropping funnel was added 400 g water and 50 g 30% hydrochloric acid in the course of 1 hour (the increased acidity of the medium facilitated separation of the organic layer). During hydrolysis a temperature of 30-40° was maintained by cooling of the flask with iced water. The product of hydrolysis was charged into a separating funnel, the aqueous solution of magnesium salts was separated, and the toluene solution was washed with hot water until neutral to congo. The solvent was then distilled off together with the volatile products through a Vigreux condenser (height 300 mm) until the temperature of the liquid had risen to 210°. Yield of residual liquid consisting of polyethylsiloxane 68.5 g (72% of the theoretical calculated on the silicon tetrachloride). The remaining ethoxyl groups were split off by treatment of the liquid with aluminosilicate [3]. Purification was effected with activated carbon. The polyethylsiloxane was then analyzed.

Found %: Si 27.2; C 47.8; H 10.2. $[(C_2H_5)_2SiO]_x$. Calculated %: Si 27.4; C 47.0; H 9.8.

Results of experiments carried out with various ratios of silicon tetrachloride to ethanol are presented in Table 1.

TABLE 1

Etherification charge			% yield of mixture of chloroethers	Alkylation charge (in g)				% yield polyethylsiloxane	
	ethanol								
$SiCl_4$ (in g)	(g)	moles per mole $SiCl_4$		Magnesium	Mixture of chloroethers	Ethyl chloride	Toluene	On $SiCl_4$	On mixture of chloroethers
680	248	1.35	85.2	43.5	150	143	327	44.0	52.0
680	248	1.35	85.2	43.5	150	143	327	60.0	69.0
520	212	1.50	87.5	44.5	150	136	327	72.0	82.5
255	104	1.50	93.6	22.0	75.6	71	236	74.0	83.0
423	183	1.60	83.2	43.5	150	143	327	72.0	89.0
340	161	1.75	81.0	29.0	100	94	218	70.0	77.4
340	184	2.00	75.0	19.0	65.2	60	90	71.0	95.0
255	138	2.00	78.0	17.1	58.7	55.2	158	72.0	92.0

Partial etherification of methyltrichlorosilane. Apparatus and procedure were the same as for etherification of silicon tetrachloride. Starting from 897 g of methyltrichlorosilane and 332 g of anhydrous ethanol, the yield of mixture of methylethoxychlorosilanes was 874 g (91% of theory on basis of reaction (4).

TABLE 2

Charge for etherification			% yield of mixture of chloroethers	Charge for alkylation (in g)				% yield of liquid	
	ethanol								
CH_3SiCl_3	(g)	moles per mole CH_3SiCl_3		Magnesium	Mixture of chloroethers	Ethyl chloride	Toluene	On CH_3SiCl_3	On mixture of chloroethers
149.5	50.6	1.1	89.3	13.2	72.2	40.7	95.4	75.3	85.2
149.5	50.6	1.1	89.3	13.0	71.0	40.2	94.0	76.6	86.0
897	332	1.2	83.5	41.5	280	144	215	95.0	99.0
897	332	1.2	89.0	23.0	140	70	164	81.5	94.5
897	332	1.2	91.0	28.8	146	82.2	192	85.3	94.2
149.5	69	1.5	86.4	12.5	70.0	38.4	90.1	80.4	94.3
149.5	69	1.5	88.7	13.0	72.7	39.9	93.5	85.0	96.0

Ethylation of products of partial etherification of methyltrichlorosilane and hydrolysis of the mixture of products of ethylation. Apparatus and procedure were the same as for the products of partial etherification of silicon tetrachloride. Into the flask was charged 28.8 g magnesium turnings, and addition was then made of a mixture of 2 ml ethyl chloride and 2 ml diethyl ether. Addition was then commenced at a uniform rate of a mixture of 146 g of products of partial etherification of methyltrichlorosilane, 82.2 g of ethyl chloride, 192 g of toluene and 2 ml of diethyl ether. The resultant mixture was hydrolyzed with 250 ml water, the product of hydrolysis was washed with water, and the solvent was distilled off. Yield of liquid consisting of polymethylethylsiloxane 75 g (85.3% of the theoretical on the basis of methyltrichlorosilane).

Elementary analysis of the polymethylethylsiloxane was performed after treatment with aluminosilicate and purification with carbon.

Found %: Si 31.54; C 40.9; H 9.00 $[CH_3C_2H_5SiO]x$. Calculated %: Si 31.8; C 40.9; H 9.09.

Table 2 contains data for experiments on etherification and ethylation when using various ratios of methyltrichlorosilane to ethanol.

SUMMARY

1. Chloroethers of orthosilicic acid (ethoxychlorosilanes) as well as substituted chloroethers (methylethoxychlorosilanes) are capable of forming organomagnesium compounds.

2. Silicon tetrachloride and methyltrichlorosilane can be alkylated by first carrying out their partial etherification and then reacting the resultant mixture with magnesium and ethyl chloride in a medium of toluene. Hydrolysis of the products of alkylation gives liquid polydiethylsiloxanes and polymethylethylsiloxanes in yields of 80-90%. It was established that the optimum yield in the alkylation of the products of partial etherification requires etherification of 40-50% of the chlorine atoms in the molecule of silicon tetrachloride or methyltrichlorosilane.

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THE SYNTHESIS OF METHYLETHYLETHOXYCHLOROSILANE AND DETERMINATION OF ITS THERMAL STABILITY

K. A. Andrianov, S. A. Golubtsov and N. P. Lobusevich

In the preceding Communication [1] we showed that the introduction of an organic radical into the molecule of an alkoxychlorosilane greatly increases the resistance of the compound to symmetrization at elevated temperature. It was shown that the degree of symmetry of arrangement of the chlorine atoms is a very important factor for the thermal stability, the alkoxyl groups playing a minor part in this connection.

We prepared a new compound – methylethylethoxychlorosilane – with the objective of ascertaining the influence of introduction of a second radical upon the thermal stability of a compound. The new compound was synthesized by ethylation of methylethoxydichlorosilane by the Grignard reaction. According to data of M. N. Kalinin [2] a chlorine atom in an alkoxychlorosilane enters into reaction with an organomagnesium compound with greater facility than does the alkoxy group. A similar phenomenon is observed in the alkylation of a substituted alkoxychlorosilane. Of the two possible reactions of methylethoxydichlorosilane

$$\begin{gathered} CH_3SiCl_2OC_2H_5 + Mg + C_2H_5Cl \rightarrow \\ CH_3(C_2H_5)SiClOC_2H_5 + MgCl_2, \end{gathered} \tag{1}$$

$$\begin{gathered} CH_3SiCl_2OC_2H_5 + Mg + C_2H_5Cl \rightarrow \\ CH_3(C_2H_5)SiCl_2 + C_2H_5OMgCl \end{gathered} \tag{2}$$

the second fails substantially to take place (methylethyldichlorosilane is not found among the reaction products).

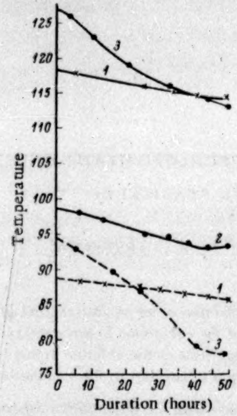
For confirmation of this characteristic, we performed the analogous ethylation reaction with methyldiethoxychlorosilane:

$$CH_3SiCl(OC_2H_5)_2 + Mg + C_2H_5Cl \rightarrow CH_3(C_2H_5)Si(OC_2H_5)_2 + MgCl_2, \tag{3}$$

$$CH_3SiCl(OC_2H_5)_2 + Mg + C_2H_5Cl \rightarrow CH_3(C_2H_5)Si(OC_2H_5)Cl + C_2H_5OMgCl. \tag{4}$$

In this case there is likewise no substitution of the alkoxyl group [reaction (4)].

Methylethoxychlorosilane, prepared by reaction (1), was subjected to thermal rearrangement by heating in the still of a rectifying column at the boiling point. For comparison with previously prepared compounds, it was also tested by heating at a temperature (in the liquid) of 100° (a vacuum was periodically created in the column for observation of the boiling point). Just as in the case of the methylethoxychlorosilanes previously described by us, the process of thermal rearrangement of methylethoxychlorosilane went extremely slowly, and after 50-hours heating we were unable to isolate individual products of rearrangement. The quantity of volatile products formed after that period was very small. In accordance with the earlier procedure [1], the index of thermal stability was taken to be the rate of change of temperature in the dephlegmator of the column. In the diagram are plotted the results that we obtained for methylethylethoxychlorosilane (curve 1) in comparison with methylethoxydichlorosilane (curve 2) and methyldiethoxychlorosilane (curve 3) at the boiling point as well as at a still temperature of 100° (broken plots). It may be suggested that the introduction of a second organic radical leads to insignificant additional stability of the compound.



Rate of change of temperature in the dephlegmator of the column. (Details in text).

The presence in the molecule of two radicals (with unsymmetrical arrangement of the chlorine atom and the ethoxy group) causes this compound to resemble methylethoxydichlorosilane in thermal stability (the latter compound has a symmetrical arrangement of the chlorine atoms).

EXPERIMENTAL

Methylethoxydichlorosilane (b.p. 99-99.5°, n_D^{20} 1.380, d^{20} 1.068) and methyldiethoxychlorosilane (b.p. 126.5-127.5°, n_D^{20} 1.393, d^{20} 1.010) were prepared by the method described previously [1]. Magnesium was used in the form of turnings not more than 0.1 mm thick.

Methylethylethoxychlorosilane. 40.6 g magnesium was charged into a flask equipped with stirrer (sealed), dropping funnel and reflux condenser. The flask was heated to 40°, and gradual addition of a mixture of 265 g methylethoxydichlorosilane, 107 g ethyl chloride and 250 g ether was commenced from the dropping funnel. Introduction of the mixture was completed in 3-4 hours, after which the reaction mass was heated on a water bath at 50° for 3 hours. After cooling, the reaction mass was transferred to a Wurtz flask for distillation of the liquid from the precipitate of magnesium salts. 215 g of the distilled liquid was fractionated from a flask with a column, and 95 g ether and 120 g residue (mixture of products of alkylation) were obtained. Rectification of 110 g of the latter in a column with a diameter of 30 mm and height of 750 mm, packed with porcelain rings, gave the following fractions:

1) 52-98°, 7.2 g (6.5%), Cl 37.5%; 2) 98-99°, 2.1 g (1.9%), Cl 44.2%; 3) 99-118°, 14.3 g (13.0%), Cl 27.6%; 4) 118-119°, 34.7 g (31.5%), Cl 23.4%; 5) 119-120°, 15.8 g (14.3%), Cl 21.6%; 6) 120-157°, 11.4 g (10.3%), Cl 13.6%; residue 14.7 g (13.3%), Cl 3.9%; losses 9.8 g (8.2%).

The 118-119° (752 mm) fraction has n_D^{20} 1.4135, d^{20} 1.062, MR_D 38.15; calcd. 38.45; it is methylethylethoxychlorosilane.

Found %: SiO_2 39.0, 39.1; Cl 23.4, 23.5; OC_2H_5 28.9, 29.2. $C_5H_{13}SiClO$. Calculated %: SiO_2 39.4; Cl 23.2; OC_2H_5 29.3.

Fraction 2) contains 44.2% chlorine and is pure methylethoxydichlorosilane (calculated: 44.3% chlorine); this testifies to the absence of methylethyldichlorosilane (b.p. 99°, % Cl 49.5).

Methylethyldiethoxysilane. Alkylation of methyldiethoxychlorosilane was performed by a similar procedure. Two experiments, starting with 300 and 249 g of methyldiethoxychlorosilane, gave 247 g of a mixture of products of alkylation. Rectification of this mixture gave the fractions:

1) 80-119°, 3.8 g (1.5%), Cl 14.5%; 2) 119-120°, 0.8 g (0.3%), Cl 23%; 3) 120-125°, 4.1 g (1.7%), Cl 17.3%; 4) 125-127° 2.9 g (1.2%), Cl 14.1%; 5) 127-131°, 7.7 g (3.1%), Cl 8.5%; 6) 131-132.5°, 15.9 g (6.5%); Cl 15.2%; 7) 132.5-134°, 12.6 g (5.1%), Cl 11.4%; 8) 134-135°, 129.3 g (52.4%); Cl – traces; 9) 135-137°, 24.3 g (9.8%); Cl 0.8%; Residue 30.2 g (12.2%). Cl 1.2%; losses 15.4 g (6.2%).

The 134-135° (754 mm) fraction, n_D^{20} 0.8440, d^{20} 1.3925, MR_D 45.45 (calcd. 45.69), is methylethyldiethoxysilane.

Found %: SiO_2 36.9, 37.0; OC_2H_5 56.3, 56.6. $C_7H_{18}SiO_2$. Calculated %: SiO_2 37.1; OC_2H_5 55.5.

Calculations on the basis of the analyses of the fractions indicate a content of 184 g methylethyldiethoxysilane and less than 4.6 g methylethylethoxychlorosilane.

Rearrangement of methylethylethoxychlorosilane. a) At the boiling point. Into the flask of the above-mentioned rectifying column was charged 68 g of methylethylethoxychlorosilane. The column was operated with full reflux at a temperature in the flask of 119°; in the course of 50-hours operation the temperature in the dephlegmator of the column gradually fell from 118° to 114.3° (curve 1). Rectification of the products of rearrangement gave the following fractions:

1) 114.3-118°, 2.4 g (3.5%), Cl 25.0%; 2) 118-119°, 41.6 g (61.2%), Cl 23.1%; residue 20.0 g (29.4%), Cl 18.5%; losses 4.0 g (5.9%).

The 1st fraction, judging by its chlorine content, is a mixture of 93% of methylethylethoxychlorosilane and 7% of methyldiethylchlorosilane (the latter is equivalent to 0.24% methylethyldichlorosilane calculated on the whole mixture).

b) At 100°. Into the flask of the column was charged 54 g methylethylethoxychlorosilane. A low vacuum was established and the flask was gradually heated to 100°. The liquid was made to boil by maintaining a residual pressure of 412 mm. The temperature in the flask was held at 100° for 50 hours, and the vacuum for determination of the change of boiling point was established periodically. After heating for 50 hours, the temperature in the dephlegmator fell from 88.5 to 85.5° (curve 1, broken). Rectification of the liquid gave the following fractions:

1) 115-118°, 3.4 g (6.3%), Cl 24.1%; 2) 118-119°, 28.2 g (52.2%), Cl 23.6%; residue 18.5 g (34.3%), Cl 21.4%; losses 3.9 g (7.2%).

Judging by the analytical data, the first fraction is a mixture of 97% methylethylethoxychlorosilane and 3% methylethyldichlorosilane (corresponding to 0.2% methylethyldichlorosilane in the whole of the starting mixture).

SUMMARY

1. Two new compounds – methylethylethoxychlorosilane and methylethyldiethoxysilane – were synthesized.

2. Ethylation of methylethoxydichlorosilane and methyldiethoxychlorosilane proceeds almost entirely in the direction of substitution of the chlorine atoms linked to the silicon; there is substantially no interaction of ethoxyl groups with the organomagnesium compound.

3. The presence of two organic radicals at the silicon atom stabilizes the molecule of substituted unsymmetrical alkoxychlorosilane to the same extent as the presence of one radical when the chlorine atoms are symmetrically arranged.

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INVESTIGATIONS IN THE FIELD OF ALKOXYSILANES

VII. THE REACTION OF TETRAACETOXYSILANE WITH ALCOHOLS. THE SYNTHESIS OF TETRAALKOXY- AND ALKOXYACETOXYSILANES*

B. N. Dolgov, V. P. Davydova and M. G. Voronkov

In 1868 Friedel and Ladenburg [2] first obtained tetraacetoxysilane (silicoacetic anhydride) by the action of acetic anhydride or acetic acid on silicon tetrachloride. These authors also showed that tetraacetoxysilane decomposes upon heating to 160-170° with the formation of acetic anhydride:

$$[\mathrm{CH_3COO}]_4\mathrm{Si} \rightarrow 2[\mathrm{CH_3CO}]_2\mathrm{O} + \mathrm{SiO_2} \qquad (1)$$

By reaction with ethyl alcohol, ethyl acetate is formed quantitatively.

$$(\mathrm{CH_3COO})_4\mathrm{Si} + 4\mathrm{C_2H_5OH} \rightarrow \mathrm{Si(OH)_4} + 4\mathrm{CH_3COOC_2H_5}. \qquad (2)$$

Furthermore, tetraacetoxysilane, as well as other silicoanhydrides of monobasic and dibasic carboxylic acids, have been repeatedly described in the literature [3-14]. In particular, they have been proposed as acylating agents for the preparation of aromatic, aliphatic-aromatic [6, 15], and heterocyclic [18, 20] ketones and also of aromatic [17] and heterocyclic [19] ketoacids. The use of tetraacetoxysilane for the synthesis of α, β-unsaturated acids [11, 16] by way of its condensation with aldehydes has been described. K. D. Petrov [6, 7] showed that tetraacyloxysilanes react with phenol according to equation (2), forming the phenyl esters of the corresponding acids. Comparatively recently there have been indications [9, 21] of the possibility of reaction of acyloxysilanes with alcohols according to equation (3) with the formation of alkoxysilanes and acetic acid.

$$\rangle\mathrm{Si{-}OOCCH_3} + \mathrm{ROH} \rightarrow \rangle\mathrm{Si{-}OR} + \mathrm{CH_3COOH}. \qquad (3)$$

Such a course of reaction in the case of tetraacetoxysilane should lead to the formation of tetraalkoxy- and alkoxyacetoxysilanes.

$$(\mathrm{CH_3COO})_4\mathrm{Si} + n\mathrm{ROH} \rightleftarrows (\mathrm{CH_3COO})_{4-n}\mathrm{Si(OR)}_n + n\mathrm{CH_3COOH} \qquad (4)$$
$$(n = 1 - 4).$$

The contradictory nature of the data in the literature relative to the character of the reaction of tetraacetoxysilane with alcohols and phenols impelled us to study this reaction in more detail.

We have demonstrated that tetraacetoxysilane reacts exothermally, even in the cold, with primary and secondary alcohols and phenols according to equation (4), forming in good yield, depending on the proportion of the reactants, tetraalkoxysilanes or alkoxyacetoxysilanes. It should be noted, however, that the compounds mentioned are formed smoothly only when the acetic acid produced is removed by distillation in vacuo and, preferably, in the absence of excess alcohol. When the acetic acid is distilled off at ordinary pressure or the reaction mixture is preheated, the yields of alkoxy derivatives drop sharply to zero and the corresponding alkyl acetates and a silicopolymer gel are formed, which points to a course of reaction analogous to equation (2). This can be explained by the fact that reaction (4) becomes reversible at temperatures above 80-90° and the acetoxysilanes acetylate the alcohol present in the reaction mixture to its acetate. It is also probable that the ester is formed by esterification of the alcohol with acetic acid, with $(CH_3COO)_{4-n}Si(OR)_n$ playing the role of a water removing agent. However, against this idea is the fact that in the reaction of tetraacyloxysilanes with phenols the corresponding esters of the latter are formed [6, 7], while it is known that phenol is not directly esterified with carboxylic acids. Both of the schemes proposed for the formation of esters in the reaction of tetraacetoxysilane with alcohols are corroborated by the fact that tetraethoxysilane upon heating with acetic acid forms silicopolymers, starting with hexaethoxydisiloxane and ending with polydiethoxysiloxane, and finally silica gel [22, 23]. At the same time, the very difficultly acetylated tert-butyl alcohol does not form tert-butyl acetate even upon prolonged boiling with tetraacetoxysilane, and the reaction proceeds only according to equation (4).

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* See previous communication [1]

The formation of esters as a result of the acetylation of the alcohols by acetic anhydride produced by thermal decomposition of the acyloxysilanes, for example according to equation (1), seems to us very improbable.

Tertiary alcohols react with tetraacetoxysilane with considerably more difficulty than the primary and secondary ones. Thus, when tert-butyl alcohol is mixed with tetraacetoxysilane, heat is not evolved and it is necessary to heat the reaction mixture to 100-140° to obtain tert-butoxyacetoxysilanes. Efforts to substitute tert-butoxy groups for more than three acetoxy groups in tetraacetoxysilane do not succeed [when tri-(tert-butoxy) acetoxysilane was boiled for 50 hours with a two-fold excess of tert-butyl alcohol, we did not observe the production of tetra-(tert-butoxy) silane)]. It is interesting to note that sec-octyl alcohol behaves similarly to the tert-butyl, in contrast to the lower secondary alcohols, and forms only tri-(sec-octoxy) acetoxysilane with tetraacetoxysilane.

It is difficult to obtain tetramethoxysilane by the reaction of tetraacetoxysilane with methyl alcohol, since a mixture of acetic acid (b.p. 118°) and silicomethyl ether (b.p. 121°) is produced that is practically inseparable by distillation.

The data obtained show that the reaction of tetraacetoxysilane with alcohols and phenols is a simple and convenient method for the synthesis of tetraalkoxy (aroxy)- and alkoxyacetoxysilanes. It can be especially recommended for the synthesis of silicoorganic compounds having the tert-butoxy group on the silicon atom, which are difficult to obtain by other methods [24], and also of compounds having unlike alkoxy groups on the silicon atom. By this method 8 tetraalkoxysilanes were synthesized, whose physical properties, yields, and analytical data are given in Table 1. Similar data are presented in Table 2 for 6 alkoxyacetoxysilanes that were synthesized (all of these compounds were previously unknown).

EXPERIMENTAL

Starting reagents. Tetraacetoxysilane was obtained by the reaction of silicon tetrachloride with acetic anhydride [13]. The tetraacetoxysilane produced was washed twice with acetic anhydride, then with absolute ether, carefully filtered off, and dried in a vacuum. After recrystallization from ether, it melted at 110°. Yield 84% calculated on the $SiCl_4$ used.

Found %: Si 10.62, 10.70. Calculated %: Si 10.63.

The starting alcohols (except ethyl) were purified by double distillation over metallic calcium. The ethyl alcohol was dehydrated by double distillation with silicoethyl ether in the presence of sodium ethylate.

Methods of synthesis. All of the syntheses were carried out in a 250-ml three-neck, round-bottom flask equipped with a stirrer with a mercury seal, a dropping funnel, a thermometer, and a reflux condenser protected with a calcium chloride tube. The tetraacetoxysilane was placed in the flask and the appropriate alcohol was introduced into it dropwise, with stirring, over the course of 15-30 minutes. In the case of primary and secondary alcohols the temperature usually rose to 50-70°. After stirring for 1.5-2 hours the reaction product was separated by fractional distillation of the reaction mixture in vacuo and was purified by a second distillation. When we attempted to remove the acetic acid by distillation at atmospheric pressure, a viscous polymer or silica gel was obtained, and the reaction product appeared to be the corresponding ester of acetic acid.

TABLE 1

Physical Properties, Analytical Data and Yields of Tetraalkoxysilanes

Name of substance	Boiling point	Pressure (mm)	n_D^{20}	d_4^{20}	MR_D		Content (in %)						Yield (in %)
							Si		C		H		
					Calculated	Found	Calculated	Found	Calculated	Found	Calculated	Found	
Tetraethoxysilane	166°	764	1.3836	0.9447	51.84	51.51	—	—	—	—	—	—	53
Tetrapropoxysilane	115	16	1.4010	0.9117	70.36	70.46	10.63	10.69, 10.42	54.50	54.66, 54.62	10.67	10.75, 10.67	80
Tetraisopropoxysilane	81—81.5	17	1.3845	0.8772	70.36	70.67	10.63	10.62, 10.58	54.50	54.41, 54.56	10.67	10.69, 10.71	77
Tetrabutoxysilane	148.8	8	1.4131	0.8996	88.88	88.85	8.64	8.66, 8.69	59.96	59.85, 60.07	11.33	11.30, 11.39	77
Tetraisobutoxysilane	129.5—130	12	1.4064	0.8855	88.88	88.97	8.64	8.63, 8.73	59.96	59.98, 60.03	11.33	11.22, 11.26	73
Tetra-(sec-butoxy) silane	116.5—117.5	10	1.4075	0.8880	88.88	88.94	8.64	8.65, 8.43	59.96	59.83, 59.58	11.33	11.16, 11.14	83
Tetraoctoxysilane	253—255	5	1.4385	0.8773	162.96	163.22	5.15	5.14, 5.45	70.52	70.39, 70.19	12.57	12.61, 12.51	87
Tetraphenoxysilane	m.p. 48	—	—	—	—	—	7.01	7.14, 7.20	—	—	—	—	81

TABLE 2

Physical Properties, Analytical Data and Yields of Alkoxyacetoxysilanes

Name of substance	Boiling point	Pressure (mm)	n_D^{20}	d_4^{20}	Molecular weight		MR_D		Ester number		Si (in %)		Yield (in %)
					Calculated	Found	Calculated	Found	Calculated	Found	Calculated	Found	
Tri-(tert-butoxy)acetoxysilane	94.5—95°	3	1.4023	0.9404	306.48	278.3, 299.0	79.62	79.41	183.0	177.6, 180.0	9.16	9.17, 9.06	76
Di-(tert-butoxy)diacetoxysilane	102.3—102.5	5	1.4040	1.0196	293.25	—	70.36	70.33	272.8	272.3, 267.3	9.58	9.66, 9.37	47.5
tert-Butoxytriacetoxysilane	104—105, m.p. 28°	4	—	—	278.3	269.5, 272.9	—	—	647.2	649, 652.8	10.09	10.56, 10.65	53
tert-Butoxy-n-butoxydiacetoxysilane	128—130	12	1.4055	1.0140	293.25	—	70.36	71.11	272.8	269.16, 265.2	9.58	9.46, 9.49	76
Dibutoxydiacetoxysilane	144—146	13	1.4099	1.0223	293.25	—	70.36	71.05	272.8	273.56, 275.1	9.58	9.39, 9.42	92
Tri-(sec-octoxy)acetoxysilane	198.7—199.7	3	1.4291	0.9064	474.8	456.7, 463.8	135.06	135.18	118.6	123.2, 120.4	5.90	5.78, 6.01	85

Analysis. The carbon, hydrogen, and silicon content of the tetraalkoxysilanes was determined on one weighed sample by combustion in a current of oxygen.* The silicon content of the alkoxyacetoxysilanes was determined by mineralization of a weighed sample of the material with a mixture of nitric and sulfuric acid (1 : 3). The ester numbers were determined for the dialkoxydiacetoxysilanes and the alkoxytriacetoxysilanes by titrating a weighed portion of the material, dissolved in a mixture of equal parts of acetone and water, with 0.2N NaOH [25] (indicator-thymol blue). The ester numbers for the trialkoxyacetoxysilanes could be determined only by heating a weighed portion in a 0.5N solution of KOH in diethyleneglycol and subsequent titration of the excess alkali with 0.5N HCl [26] (indicator-thymolphthalein). Representative experiments are described below.

Synthesis of tetra-n-butoxysilane. To 54.2 g of tetraacetoxysilane, 68.4 g of n-butyl alcohol was added rapidly, with stirring; the temperature of the mixture rose to 60° and all of the tetraacetoxysilane went into solution. After stirring for a half hour, the mixture was subjected to fractional distillation in vacuo. 50.5 g of tetrabutoxysilane was obtained with b.p. 136° (5 mm), and after a second distillation 148.8° (8 mm), d_4^{20} 0.8996, n_D^{20} 1.4131. Yield 77%. Literature data [27]: b.p. 163° (20 mm), n_D^{20} 1.4131, d_4^{20} 0.913.

Synthesis of tetra-sec-butoxysilane. Upon the addition of 28 g of sec-butyl alcohol to 25 g of tetraacetoxysilane, the temperature rose to 60°. After stirring for an hour, the mixture was subjected to fractional distillation in vacuo. Tetra-sec-butoxysilane was obtained with b.p. 116-118° (8 mm); after redistillation the b.p. was 116.5-117.5° (10 mm), d_4^{20} 0.8880, n_D^{20} 1.4075. Yield 23 g (83%).

Synthesis of tri-(tert-butoxy)acetoxysilane. 65 g of tetraacetoxysilane was mixed with 91 g of tert-butyl alcohol. The temperature of the mixture dropped to +15°. After heating to boiling for 2 hours, with stirring, the temperature of the reaction mixture rose to 135°. The excess alcohol and the acetic acid which was formed were distilled off at atmospheric pressure. When the residue was fractionally distilled in vacuo, 48 g of tri-(tert-butoxy)acetoxysilane was obtained with b.p. 96.5-97° (4 mm). Yield 63%.

In another experiment the molecular ratio of the reactants was 1 : 3.5 and the reaction mixture was heated, with stirring, for 4 hours to 100°. Under these conditions the yield of tri-(tert-butoxy)acetoxysilane with b.p. 103.5-104° (8 mm) rose to 76%.

In an exactly analogous manner, but with a molar ratio of tetraacetoxysilane to tert-butyl alcohol of 1 : 2 and 1 : 1, the corresponding di-(tert-butoxy)diacetoxysilane (yield 48%) and tert-butoxytriacetoxysilane (yield 53%) were obtained, with properties shown in Table 2.

Attempt to prepare tetra-tert-butoxysilane. 25.5 g of tri-(tert-butoxy)acetoxysilane was heated to boiling with 12.3 g of tert-butyl alcohol for 50 hours (temperature of reaction mixture 130-140°). On fractional distillation in vacuo, 10 g of tert-butyl alcohol and 20 g of unchanged tri-(tert-butoxy)acetoxysilane were obtained. A viscous tar remained in the distilling flask.

Synthesis of tert-butoxy-n-butoxydiacetoxysilane. a) 11 g of n-butyl alcohol was added to 41.5 g of tert-butoxytriacetoxysilane; after fractional distillation in vacuo, 21 g (50%) of tert-butoxy-n-butoxydiacetoxysilane was obtained with b.p. 128-130° (12 mm) (Table 2).

b) 19 g of tert-butyl alcohol was added dropwise, with stirring, to 66 g of tetraacetoxysilane. The mixture was warmed carefully for a half hour until the tetraacetoxysilane completely dissolved. After cooling, 19 g of n-butyl alcohol was added. The temperature of the mixture thereupon rose to 70°. After stirring for 2 hours and subsequent fractional distillation in vacuo, 57.2 g of tert-butoxy-n-butoxydiacetoxysilane was obtained with b.p. 128-130° (12 mm), identical with the compound described above. Yield 70%; n_D^{20} 1.4055, d_4^{20} 1.0140.

Synthesis of tetraphenoxysilane. 41 g of freshly distilled phenol in 50 ml of dry benzene was added to 27 g of tetraacetoxysilane. The temperature of the mixture rose to 30°. After stirring at 100° for 2 hours, the benzene and acetic acid were distilled off from the reaction mixture in vacuo. After cooling, the residue solidified to a crystalline mass. One recrystallization from ethyl ether yielded 40 g of tetraphenoxysilane with m.p. 48°. Yield 81%.

Reaction of tetraacetoxysilane with methyl alcohol. 21.0 g of methyl alcohol was added slowly to 43.0 g of tetraacetoxysilane, while cooling with ice water and stirring. During this process all of the tetraacetoxysilane went into solution. Upon vacuum distillation of the reaction mixture at 22-34° (10 mm), there distilled off a mixture of tetramethoxysilane and acetic acid (59 g) which was inseparable by distillation. There was 5 g of residue in the flask.

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* The analyses were made by Yu. N. Platonov, to whom the authors express their appreciation.

Preparation of n-propyl acetate by the reaction of tetraacetoxysilane with n-propyl alcohol. 27.1 g of n-propyl alcohol was added to 26.5 g of tetraacetoxysilane. The temperature of the mixture rose to 53°. When the reaction mixture was gradually heated, a transparent gel separated at 95°. Upon distillation of the liquid products, n-propyl acetate (b.p. 101.5-102°) was obtained in high yield.

SUMMARY

A new method has been developed for the synthesis of tetraalkoxy- and tetraaroxysilanes, and also of alkoxyacetoxysilanes by means of the reaction of tetraacetoxysilane with alcohols and phenols. By this method 6 alkoxyacetoxysilanes not previously described in the literature were obtained, as well as 7 tetraalkoxysilanes and tetraphenoxysilane. It has been shown that at temperatures above 80-90° tetraacetoxysilane reacts with alcohols to form the corresponding esters.

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DIRECT SYNTHESIS OF NAPHTHYLTRICHLOROSILANE

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α-Naphthyltrichlorosilane was first prepared in 1908 [1] by synthesis through the organomagnesium compound. However, up to the present time it has not been utilized at all in the synthesis of organosilicon compounds containing the naphthyl radical, for example in preparing α-naphthyltrialkylsilanes, a few representatives of which have been obtained from α-naphthyltriethoxysilane [2]. Introduction into synthetic practice of α-naphthyltrichlorosilane, containing chlorine atoms which are comparatively more reactive than the ethoxy group, can considerably broaden the possibility of investigating the α-naphthyl-containing organosilicon compounds, which have not been sufficiently studied.

The small yields of α-naphthyltrichlorosilane obtained by the method described in [1] prompted us to undertake an experiment on its preparation by direct synthesis. The possibility of direct synthesis of alkyl- and arylhalogen silanes was first shown by Rokhov [3]; for example he investigated the use of different catalysts for the reaction of C_6H_5Cl with Si [4] and concluded that silver was the best catalyst to use in the direct synthesis with aryl halides; this has been confirmed in our study of the reaction of α-chloronaphthalene with silicon.

We have established that α-$C_{10}H_7Cl$ reacts with silicon in the presence of copper (Si-Cu alloy) with low yields (1-2%) even at 600°; addition to the alloy of Ag_2O to the extent of 20% by weight increased the yield of naphthyltrichlorosilane to 10-12%; in this case the reaction is accompanied by the formation of $SiCl_4$ (2-3%) and naphthalene (10-15%). Still higher yields were obtained when Si-Cu alloy containing 20% Ag_2O was used and dry HCl was passed through the reaction tube; the yield of the desired product increased with this procedure to 25%; in this case $SiHCl_3$ was obtained as a byproduct, as well as $SiCl_4$ and naphthalene. Under these conditions naphthyltrichlorosilane was formed in comparatively small amounts (6-7%) at temperatures below 500°; at 500-540° the yield increased to 24-25%, but at higher temperatures it decreased. Speed of addition of the chloronaphthalene and pulverization of the alloy were of essential importance; best results were obtained when the rate of addition was 8-10 g/hr and the alloy was finely pulverized.

EXPERIMENTAL

The reaction of α-chloronaphthalene with silicon was carried out in a porcelain tube 650 mm long and 24 mm in diameter, which was heated in an obliquely positioned electric furnace; the temperature was measured with a thermocouple; the reaction products were collected in a chilled container connected with a reflux condenser. The condensate, usually dark in color, was fractionally distilled in vacuo, using a herringbone dephlegmator in the beginning; a fraction with b.p. 127-133° at 3 mm (containing 96% $C_{10}H_7SiCl_3$) was obtained along with byproducts, the yields of which per 100 g of α-chloronaphthalene are given in the table.

By redistillation of the fraction boiling at 127-132° at 3 mm on the column, a pure product was obtained which consisted of a liquid with b.p. 148° at 4 mm.

Found %: Cl 40.30. $C_{10}H_7SiCl_3$. Calculated %: Cl 40.62.

By treatment of the naphthyltrichlorosilane with an excess of C_2H_5MgBr a substance was obtained which boiled at 132-133° (3 mm), d_4^{20} 0.9734, n_D^{20} 1.5712.

Found %: C 79.23; H 9.20; Si 11.49. $C_{10}H_7Si(C_2H_5)_3$. Calculated %: C 79.26; H 9.15, Si 11.59.

Temperature	$SiCl_4 + SiHCl_3$ (in g)	Naphthalene (in g)	Initial products (in g)	Intermediate fraction (in g)	Fraction with b.p. 127-132° at 3 mm (in g)	Residue (in g)
480°	2	8	65	7	7	2
500	35	20	35	4	25	3
520	45	21	40	4	24	2
540	27	24	35	6	24	3
560	28	26	34	5	19	7

The analytical data confirm the production by direct synthesis of naphthyltrichlorosilane, apparently consisting of a mixture of the alpha- and beta-isomers; the formation of the β-naphthyltrichlorosilane must occur as a result of partial isomerization of the α-naphthyl radical to the β-naphthyl under the conditions of direct synthesis (high temperature, presence of HCl and Al, which always is contained in small amounts in commercial silicon). In the literature there are examples of such conversions in the presence of various reagents, particularly $AlCl_3$ or Al_2O_3 and HCl [5]. To confirm the presence of β-naphthyltrichlorosilane in the product of direct synthesis, ultraviolet absorption spectra were obtained * for α-naphthyltriethylsilane synthesized from α-naphthyltrichlorosilane and produced from the product of direct synthesis. For pure α-naphthyltriethylsilane an absorption maximum was observed at 312 millimicrons (in heptane solution); for the naphthyltriethylsilane obtained from the product of direct synthesis 2 maxima were observed at 312 and 319 millimicrons; although we did not obtain the absorption spectrum of the β-naphthyltrialkylsilanes, however by analogy with the β-alkylnaphthalenes [6], which have an absorption maximum in the region of 320 millimicrons, we may conclude that the product of direct synthesis is a mixture of α- and β-naphthyltrichlorosilanes.

SUMMARY

1. The direct synthesis of the naphthylchlorosilanes has been carried out for the first time; it has been shown that only naphthyltrichlorosilane is obtained by this method.

2. An hypothesis that there is a simultaneous partial isomerization of the α-naphthyl radical to the β-naphthyl has been confirmed by spectral analysis.

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INVESTIGATIONS IN THE FIELD OF CONJUGATED SYSTEMS

LXXIII. THE ORDER OF ADDITION OF BROMINE TO VINYLACETYLENE

A. A. Petrov, G. I. Semenov and N. P. Sopov

In an earlier publication from our laboratory it was shown on the basis of chemical data that vinylacetylene adds bromine by all three possible routes, forming the dibromides (I), (II), and (III) in the ratio 11 : 8 : 1 [1].

$$\underset{\text{(I)}}{CHBr{=}CBr{-}CH{=}CH_2},\quad \underset{\text{(II)}}{CHBr{=}C{=}CH{-}CH_2Br},\quad \underset{\text{(III)}}{CH{\equiv}C{-}CHBr{-}CH_2Br}$$

The properties of the 1,3-diene (I) isolated from the mixture proved to be identical with the properties of 1,2-dibromobutadiene-1,3 prepared in another way. The structure of the allene dibromide (II) was demonstrated by oxidation to produce bromoacetic acid. The conclusion regarding the presence in the mixture of the acetylenic dibromide (III) was less reliable. It was based on the fact that the dibromide fraction (I) reacted on the end acetylene group with an ammoniacal solution of silver oxide. However, it was shown in this same work that the allene dibromide (II) very readily split out hydrogen bromide upon reaction with alkalies (with the formation of vinylbromoacetylene), and therefore it was possible erroneously to mistake the ingredient allene dibromide (II) for the acetylenic dibromide.

Recent publications by one of us with Yu. I. Porfireva, Kh. V. Balyan and E. A. Leporskaya [2-5] have shown the peculiar mechanism of the reactions of the vinylacetylenic hydrocarbons of various structures with hydrogen, hydrogen bromide, bromine, and other reagents. In the light of these new data the results of the earlier experiments on the bromination of vinylacetylene have acquired significant interest.

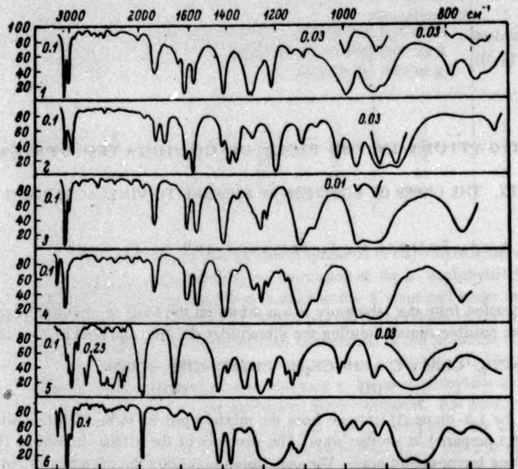
In order to obtain additional verification of the correctness of our initial conclusions concerning the structure of the isomeric dibromides of vinylacetylene, we again undertook experiments on the bromination of this hydrocarbon, subjected the mixture of dibromides to more careful fractional distillation, and studied the infrared spectra of the two principal fractions.

The results of these new experiments confirmed the earlier conclusions. It was established that the chief products of the bromination of vinylacetylene are the allene (II) and diene (I) dibromides. The acetylenic dibromide (III) is present only as a small contaminant of these two dibromides.

When the reaction temperature was lowered, the allene dibromide content of the mixture was significantly increased. There is therefore a basis for supposing that the 1,3-diene dibromide (I) originates as a result of the isomerization during the reaction process of the initially formed allene dibromide.

In the figure, absorption curves are given for the dibromide fractions with b.p. 43-46° (10 mm) (curve 4) and 69.5-70.5° (10 mm) (curve 6), and for 1,2-dibromobutadiene-1,3 (curve 3). From the figure it is apparent that the fraction with b.p. 43-46° (10 mm) is 1,2-dibromobutadiene-1,3 (characteristic intensity frequencies 6.17, 6.42, 10.32, and 10.78 μ) with a small admixture of the acetylene dibromide (characteristic frequencies 3.03, 4.67 μ). At the same time, the fraction with b.p. 69.5-70.5° (10 mm) absorbed like a typical allene compound (characteristic frequency 5.09 μ). However, this material contained a small admixture of the acetylene dibromide, since the frequencies 3.03 and 4.67 microns appeared in its spectrum.

Since the presence of the acetylenic dibromide has been established in both of the principal dibromide fractions, it can be assumed that the percentage of it in the mixture of dibromides is a little higher than previously supposed, namely of the order of 5-10%.



Absorption Spectra
1) 1-Bromobutadiene-1,3; 2) 2-bromobutadiene-1,3; 3) 1,2-dibromobutadiene-1,3; 4) fraction b.p. 43-46°; (10 mm) of vinylacetylene dibromides; 5) 4-chlorobutadiene-1,2; 6) fraction b.p. 69.5-70.5° (10 mm) of vinylacetylene dibromides.

For the sake of greater assurance in our conclusions concerning the structure of the isomeric dibromides of vinylacetylene, we determined the infrared spectra of 1- and 2-bromobutadiene-1,3 and also of 4-chlorobutadiene-1,2 for purposes of comparison. The infrared spectra of the diene bromides and the allene halogen derivatives have not previously been described in the literature. All these spectra are presented in the figure. The predominant frequencies found in the spectra of 1- and 2-bromo- and 1,2-dibromobutadiene-1,3 are given in the table. The frequencies are compared with those accepted for divinyl [6] and chloroprene [7].

Substance	${}^{\nu}CH$	${}^{\omega}C{=}C$	${}^{\delta}CH$	${}^{\gamma}CH$	$2\times{}^{\gamma}CH$
$CHBr{=}CH{-}CH{=}CH_2$.	3106 3012 —	1626 1572	1414 1305 1292	— 996 925 912	1842
$CH_2{=}CBr{-}CH{=}CH_2$.	3106 3030 2941	1621 1577	1416 1385 1284	1017 972 921 887	1842
$CHBr{=}CBr{-}CH{=}CH_2$	3105 3012 —	1621 1558	1414 1353 1282	— 969 928 —	1859

The spectrum of 2-bromobutadiene is very similar to that of chloroprene.

The vibrational frequencies for C-H bonds are represented in all three bromine derivatives with two characteristic frequencies for the vinyl groups. Bromoprene has one additional intense absorption band with simultaneous weakening of the frequency 3030 cm^{-1}.

Owing to the disturbance of the symmetry of the molecule, in the infrared spectra of the substances under investigation, both frequencies for a conjugated system of double bonds a[illegible]nt, corresponding to its symmetrical and unsymmetrical vibration. The intensity of the frequency for [illegible] unsymmetrical vibrations is higher in 1-bromobutadiene. In comparison with chloroprene and especially [illegible] divinyl in all cases a shift of the absorption band to the long-wave region is observed. The planar CH-deformations are represented by absorption bands characteristic of the trans-configuration of similar molecules [8].

All the bromides under consideration have intense absorption bands characteristic of the non-planar deformation CH-vibrations of the vinyl group (983 ± 13 and 926± 5 cm^{-1}). An intense overtone in the region 1850± 8 cm^{-1} corresponds to the second of these frequencies.

The spectrum of bromoprene is distinguished by the presence of a rather intense absorption in the region of 1770 cm^{-1}. Apparently this is an overtone of the frequency 887 cm^{-1}, which is very intense in this spectrum. In the spectrum of 1-bromobutadiene a more intense absorption is observed, in comparison with the other materials, in the region of 1669 cm^{-1}.

The valence vibrations for the C-C bonds are represented in all the spectra, apparently, by frequencies around 1200 cm^{-1}.

In the region of 3.5-5.5 μ in all the spectra, the presence is noted of many weak and very weak frequencies which probably are overtones of the frequencies lying in the region 7-10 μ.

The spectrum of 4-chlorobutadiene-1,2 is very similar to the spectra of methylallene [9] and allene [10] with respect to the position of the characteristic frequencies. On the basis of the frequency relationships given in the literature for these two hydrocarbons, the following observations can be made concerning the spectrum of 4-chlorobutadiene-1,2 [11, 12].

The CH-valence vibrations are represented here by the frequencies 3077, 3012, 2967, and 2841 cm^{-1}. In the infrared spectra of allene and methylallene a frequency around 3060 cm^{-1} was not observed, but it occurs in the Raman spectra of both compounds. The frequency 2841 cm^{-1} is possibly compound [11].

The antisymmetrical vibrations of the system $C=C=C$ are represented by the intense doublet 1965, 1922 cm^{-1}. The division of the vibration frequency of the allene system was observed earlier in the case of the allenic acids and their derivatives [13].

The absorption bands at 1445, 1397, 1326, and 1255 cm^{-1} must be referred to the CH planar deformation vibration. In the spectrum of methylallene a doublet corresponds to each of these frequencies [9]. The CH non-planar deformation frequencies are represented in the spectrum by intense absorption bands at 1014 and 932 cm^{-1}. A very intense frequency around 850 cm^{-1} can be referred to the deformation of the system $C=C=C$ or the oscillation of the CH_2 group. The absorption band at 1709 cm^{-1} is evidently the first overtone of the frequency 851 cm^{-1}.

In conclusion, it should be noted that infrared spectroscopy is the most convenient and exact method of determining the structure of the products of addition of various materials to the vinylacetylene hydrocarbons, since by it the question is answered of the character of the system of multiple bonds (conjugated diene system, allene grouping, or triple bond), each of which is represented in infrared spectra by characteristic frequencies.

EXPERIMENTAL

To a solution of 54 g of vinylacetylene in 300 ml of chloroform was added dropwise a solution of 80 g of bromine in 75 ml of chloroform with mechanical stirring at a temperature of –22-25°. Cooling was accomplished by means of a mixture of dry ice and acetone. Upon completion of the reaction the mixture was distilled initially under the vacuum of a water pump, on a water bath with the temperature no higher than 30°; after distilling off the excess vinylacetylene and most of the chloroform, an oil pump was attached and further distillation was carried out at 10 mm. A Widmer column (20-cm spiral) was employed with a dephlegmator. In this manner the following fractions were obtained: 1st) 43-36° (1,2-dibromobutadiene-1,3), 15 g; 2nd) 46-69.5°, 3.8 g; 3rd) 69.5-70.5° (1,4-dibromobutadiene-1,2), 25 g; 4th) 70.5-80°, 3.1 g; residue 26.5 g.

Repetition of the experiment at a temperature around –10° gave results no different than those published earlier.

The spectra of all the materials were determined in a double-beam IKS-2 spectrometer with an automatic recorder. The thickness of the layer was 0.1 or 0.03 mm. In the range 3-5 microns a lithium fluoride prism was used, and in the range 5-14 microns a sodium chloride prism was employed.

Infrared spectrum of fraction with b.p. 43-46° (10 mm), n_D^{20} 1.5840:* 3.03(m), 3.22(s), 3.32(m), 3.59, 4.01, 4.42(vw), 4.66(w), 4.81(vw), 5.38(s), 6.17(s), 6.42(s), 7.07(s), 7.39(w), 7.70(m), 7.80(w), 7.96(m), 8.10(m), 8.38(w), 8.56(w), 8.92(s), 9.25(m), 10.32(s), 10.78(s), 11.49(w), 11.93(w), 12.88(s), 14.28(s) μ.

Infrared spectrum of fraction with b.p. 69.5-70.5° (10 mm), n_D^{20} 1.6022: 3.04(m), 3.26(s), 3.32(m), 3.37(m), 3.53(w), 3.65(vw), 3.80(w), 3.91(vw), 4.13(vw), 4.18(w), 4.31(w), 4.40(vw), 4.50(vw), 4.68(w), 5.09(s), 5.82(w), 6.17(w), 6.40(w), 6.94(s), 7.22(s), 7.52(w), 8.35(s), 8.54(m), 8.86(m), 9.98(w), 10.30(w), 10.79(m), 11.51(s), 11.84(s), 12.85(m), 13.90(s) μ.

1-Bromobutadiene-1,3 was obtained by distilling 1,4-dibromobutene-2 with pulverized KOH [14]. It was purified by distillation through a Widmer column. B.p. 91-91.5° (758 mm), n_D^{20} 1.5160.

Infrared spectrum: 3.22(s), 3.32(s), 3.48(vw), 3.69, 3.88, 4.01, 4.16, 4.42(vw), 5.40(m), 5.73(w), 5.99(m), 6.15(s), 6.36(s), 7.07(s), 7.66(s), 7.76(s), 8.24(s), 8.71, 9.00, 9.85(w), 10.04(s), 10.81(s), 10.97*(s), 12.64(s), 13.21(s), 14.30(m) μ.

2-Bromobutadiene-1,3 was obtained by the addition of hydrogen bromide to vinylacetylene in the presence of cuprous bromide [15]. B.p. 42° (165 mm), n_D^{20} 1.4986.

Infrared spectrum: 3.22(s), 3.30(m), 3.40(s), 4.17(w), 5.14(w), 5.43(m), 5.68(m), 6.17(s), 6.34(s), 7.05(m), 7.22(s), 7.39(s), 7.79(m), 8.33(s), 8.97(s), 9.30(w), 9.83(s), 10.29(s), 10.86(vs), 11.28(vs), 13.65(m) μ.

1,2-Dibromobutadiene-1,3 was obtained from the fraction with b.p. 43-46° by treating it for 4 hours in the cold with a 10% solution of KOH in methanol [1]. After dilution of the mixture, the dibromide that separated was washed with a solution of $CaCl_2$, dried over $CaCl_2$, and distilled with a Widmer fractionating column. B.p. 43-43.5° (10 mm), n_D^{20} 1.5804.

Infrared spectrum: 3.22(s), 3.32(m), 3.59, 3.76, 4.01, 4.42, 4.81, 5.10(w), 5.38(s), 5.80(w), 6.17(s), 6.42(s), 7.07(s), 7.39(w), 7.80(w), 7.96(s), 8.10(m), 8.92(s), 9.25(m), 10.32(vs), 10.78(vs), 11.49(w), 12.89(s), 14.47(m) μ.

4-Chlorobutadiene-1,2 was obtained from vinylacetylene and hydrogen chloride [16]. It was repeatedly fractionated. B.p. 87.5-88° (758 mm), n_D^{20} 1.4778.

Infrared spectrum: 3.03(vw), 3.26(m), 3.32(s), 3.37(s), 3.52(m), 3.72, 4.01, 4.08, 4.13, 4.34, 4.56, 4.64(vw), 5.02, 5.09(s), 5.85(s), 6.92(s), 7.16(m), 7.54(s), 7.97(s), 8.18(s), 8.57(m), 8.73(s), 8.84(m), 9.86(s), 10.01(m), 10.73(s), 11.75(vs), 12.58(m), 13.80(s) μ.

SUMMARY

1. The infrared spectra of 1- and 2-bromobutadiene-1,3; 1,2-dibromobutadiene-1,3; 4-chlorobutadiene-1,2; and the two principal fractions of vinylacetylene dibromides have been studied.

2. By means of infrared spectroscopy confirmation has been obtained of the conclusions arrived at earlier on the basis of chemical data concerning the formation by the action of bromine on vinylacetylene of all three possible dibromides, with a predominance of the allene and 1,3-diene compounds.

3. It has been shown that in the bromination of vinylacetylene, when the temperature is decreased, the allene dibromide content of the mixture increases at the expense of 1,3-dienedibromide.

4. Comparison of the infrared spectra of 1-bromo-, 2-bromo-, and 1,2-dibromobutadiene-1,3 has revealed a characteristic shift of the multiple-bond frequencies toward the long wavelength region as a result of union with the bromine atom.

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* Frequencies marked by an asterisk appeared as shoulders on other frequencies. Intensity of band; vs = very strong, s = strong, m = medium, w = weak, vw = very weak.

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REACTION OF 3,3-DIMETHYLHEXYNE-1 WITH THE LOWER SATURATED MONOBASIC ACIDS

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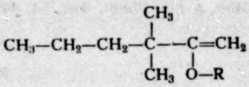
It has been shown earlier that on addition of acetic, propionic, or butyric acid to phenylacetylene, octyne-1, and its isomer 3-methyl-3-ethylpentyne-1, the appropriate monosubstituted vinyl β-esters and the corresponding ketones are produced [1-3].

In the present paper we describe the reaction of the same acids with 3,3-dimethylhexyne-1, another isomer of octyne-1, under analogous conditions (mercuric salts and boron fluoride etherate). We have isolated 2-acetoxy-3,3-dimethylhexene-1 (I), 2-propionoxy-3,3-dimethylhexene-1 (II), 2-butyroxy-3,3-dimethylhexene-1 (III), and in all cases 3,3-dimethylhexanone-2 (IV).

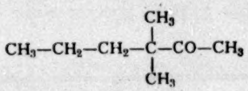


$$CH_3{-}CH_2{-}CH_2{-}\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C}}{-}\underset{\underset{\large O-R}{|}}{C}{=}CH_2$$

(I) $R{=}COCH_3$

(II) $R{=}COC_2H_5$

(III) $R{=}COC_3H_7$



$$CH_3{-}CH_2{-}CH_2{-}\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C}}{-}CO{-}CH_3$$

(IV)

The properties of product (IV) agree with the properties of the same ketone synthesized by the degradation of 2,3-dimethylhexanediol-2,3 with concentrated sulfuric acid [4]. We attempted to prepare 3,3-dimethylhexanone-2 from 3,3-dimethylhexanol-2 by oxidation of the latter with chromic acid, but from this reaction we obtained other products which we did not investigate further.

All the esters described by us were colorless, clear, mobile liquids, having an odor reminiscent of ketone (IV). In all instances we found in the first fractions of the reaction products small, variable amounts of unreacted hydrocarbon, and in all fractions, besides the esters, 3,3-dimethylhexanone-2.

The vinyl β-ethers synthesized by us were almost quantitatively hydrolyzed at 48-50° in the presence of acetic acid-semicarbazide. In the reaction products only the semicarbazone of 3,3-dimethylhexanone-2 was detected, which confirms the correctness of formulas (I), (II), and (III) given above for the esters.

EXPERIMENTAL

The starting material, dimethylpropylchloromethane, was obtained by us from the corresponding tertiary alcohol by saturation of the latter with gaseous hydrogen chloride [5]. B.p. 21-23° (10-11 mm), n_D^{20} 1.4140.

1,1-Dichloro-3,3-dimethylhexane. 45 g of vinyl chloride was liquefied with the aid of dry ice. Into the liquid vinyl chloride was run 95.8 g of dimethylpropylchloromethane (b.p. 21-23° at 10-11 mm), and 8.0 g of anhydrous aluminum chloride [6] was added during the course of 30 minutes. The reaction mixture was kept in a bath with dry ice and was stirred continuously. In an hour and a half after the introduction of the first portion of the catalyst, strong evolution of heat from the reaction mixture occurred with vigorous liberation of gaseous products, after which stirring was continued for another 30 minutes. Water and hydrochloric acid were added to the reaction products to dissolve completely the basic aluminum salts, and the mixture was then extracted with ether. The ether extract was washed with a sodium carbonate solution and dried with fused calcium chloride. The yield was 64.9 g (44.7%) of 1,1-dichloro-3,3-dimethylhexane.

B. p. 73.5-74° (8 mm), d_0^0 1.0267, d_{20}^{20} 1.0103, d_4^{20} 1.0084, n_D^{20} 1.4507, MR_D 48.59; calculated, 48.88.

Found %: Cl 38.69, 38.67. M 167. $C_8H_{16}Cl_2$. Calculated %: Cl 38.73. M 183.

3,3-Dimethylhexyne-1. 46 g of 1,1-dichloro-3,3-dimethylhexane (b.p. 73-75° at 8 mm, n_D^{20} 1.4507) was added to 26 g of fused potassium hydroxide with continuous stirring. The reaction products distilled off and were again conducted through the same alkali. The distillate was diluted with ether and dried with fused calcium chloride. The yield was 26.0 g (94%) of 3,3-dimethylhexyne-1.

B.p. 97-98.5°, d_0^0 0.7466, d_{20}^{20} 0.7301, d_4^{20} 0.7291, n_D^{20} 1.4050, MR_D 37.04. C_8H_{14} F. Calculated 37.14.

Found %: C 86.95, 87.02; H 12.82, 12.91. M 106. C_8H_{14}. Calculated %: C 87.20; H 12.80. M 110.

1-Chloro-3,3-dimethylhexene-1. The intermediate halogen-containing fractions in the synthesis of 3,3-dimethylhexyne-1 were combined and redistilled in vacuo. The yield was 6.3 g (9%) of 1-chloro-3,3-dimethylhexene-1.

B.p. 44.5-45° (9-8 mm), d_0^0 0.9103, d_{20}^{20} 0.8939, d_4^{20} 0.8925, n_D^{20} 1.4397, MR_D 43.28. $C_8H_{15}Cl$ F. Calculated 43.54.

Found %: Cl 24.13, 24.00, M 135. $C_8H_{15}Cl$. Calculated %: Cl 24.18. M 147.

2-Acetoxy-3,3-dimethylhexene-1. 26 g of glacial acetic acid, 2.6 g of acetic anhydride, and 1.7 g of mercuric oxide were heated until the oxide was completely dissolved. To the cooled solution were added 2 ml of boron fluoride etherate (b.p. 124-126.5°) and 40.0 g of 3,3-dimethylhexyne-1 (b.p. 97-98°). After stirring for 3 hours at room temperature and a half hour at 50°, the reaction mixture was diluted with ether, washed with water and with a solution of sodium carbonate, and dried with calcium chloride. The yield was 16.6 g (26.8%) of 2-acetoxy-3,3-dimethylhexene-1.

B. p. 74-75° (56 mm), d_0^0 0.8435, d_{20}^{20} 0.8290, d_4^{20} 0.8278, n_D^{20} 1.4164, MR_D 51.65. $C_{10}H_{18}O_2$ F. Calculated 49.57.

Found %: C 70.42, 70.58; H 10.74, 10.62. M 139. $C_{10}H_{18}O_2$. Calculated %: C 70.55; H 10.66. M 170.

As by-products, 5 g of high molecular weight materials was obtained which was not investigated further, and the presence of 10.0 g of 3,3-dimethylhexanone-2 was established through its semicarbazone. Traces of the starting hydrocarbon were detected in the first fraction by the formation of a precipitate of silver acetylide. The semicarbazones obtained from the initial and intermediate fractions melted at 122-123° (from alcohol) and gave no lowering of the melting point when mixed with an equal quantity of the semicarbazone obtained by the hydrolysis of the esters here described in the presence of acetic acid-semicarbazide.

Reaction of 2-acetoxy-3,3-dimethylhexene-1 with acetic acid-semicarbazide. 1.00-1.05 g of 2-acetoxy-3,3-dimethylhexene-1 (b.p. 74-75° at 56 mm) was maintained at 48° for 15 hours in a solution of acetic acid-semicarbazide [2]. The semicarbazone obtained melted at 122-123° (from alcohol). The yield was almost quantitative. According to data in the literature, the semicarbazone of 3,3-dimethylhexanone-2 melts at 119-120° [4]. The selnicarbazone of the aldehyde isomeric with the ketone was not detected.

2-Propionoxy-3,3-dimethylhexene-1. 27.4 g of propionic acid (b.p. 139-141°, n_D^{20} 1.3860) and 2.2 g of mercuric oxide were heated until the latter dissolved. To the cooled solution were added 2 ml of boron fluoride etherate and 40 g of 3,3-dimethylhexyne-1 (b.p. 97-98°). After stirring for 3 hours at room temperature and 2 hours at 50°, the reaction products were diluted with ether, washed and dried. The yield was 18 g (26.9%) of 2-propionoxy-3,3-dimethylhexene-1.

B.p. 72-73° (52 mm), d_0^0 0.8620, d_{20}^{20} 0.8468, d_4^{20} 0.8456, n_D^{20} 1.4130, MR_D 54.34. $C_{11}H_{20}O_2$ F . Calculated 54.18.

Found %: C 71.52, 71.64; H 11.04, 11.02. M 122, $C_{11}H_{20}O_2$. Calculated %: C 71.69; H 10.94. M 184.

Investigation of the fractions showed that not more than 1.5 g of the starting hydrocarbon failed to react. 11 g appeared combined as high-molecular products, and 9.8 g entered into the formation of 3,3-dimethylhexanone-2, the presence of which was established by isolation of the semicarbazone.

Reaction of 2-propionoxy-3,3-dimethylhexene-1 with acetic acid-semicarbazide [2] for 15 hours at 48° and for some days at room temperature resulted in the formation in almost quantitative yield of the semicarbazone of 3,3-dimethylhexanone-2 with m.p. 122-123° (from alcohol). The semicarbazone thus obtained gave no lowering of the melting point when mixed with equal amounts of the semicarbazones obtained from the intermediate fractions of the products of the synthesis of 2-propionoxy-3,3-dimethylhexene-1. The semicarbazone of the aldehyde isomeric with the ketone was not found.

2-Butyroxy-3,3-dimethylhexene-1. 27.5 g of butyric acid (b.p. 161-163°) and 1.7 g of mercuric oxide were heated until the latter was dissolved. To the cooled solution were added 2 ml of boron fluoride etherate and 40 g of 3,3-dimethylhexyne-1 (b.p. 97-98°). After stirring for 3 hours at room temperature and 1-1/2 hours at 50°, the reaction mixture was worked up in the usual manner. The yield was 12.0 g (16.7%) of 2-butyroxy-3,3-dimethylhexene-1.

B.p. 29-30° (5 mm), d_0^0 0.8469, d_{20}^{20} 0.8324, d_4^{20} 0.8311, n_D^{20} 1.4154, MR_D 59.80. $C_{12}H_{22}O_2$ F . Calculated 58.80.

Found %: C 72.61, 72.53; H 11.26, 11.25. M 130. $C_{12}H_{22}O_2$. Calculated %: C 72.68; H 11.18. M 198.

Reaction of 2-butyroxy-3,3-dimethylhexene-1 with acetic acid-semicarbazide. 0.5 g of 2-butyroxy-3,3-dimethylhexene-1 (b.p. 29-30° at 5 mm) was heated for 15 hours at 48° with a solution of an excess of acetic acid-semicarbazide [2]. An almost quantitative yield was obtained of the semicarbazone of 3,3-dimethylhexanone-2 with m.p. 122-123° (from alcohol), which gave no lowering of the melting point when mixed with the known semicarbazone of 3,3-dimethylhexanone-2 and with the semicarbazones obtained from the intermediate fractions of the products of the synthesis of 2-butyroxy-3,3-dimethylhexene-1. The semicarbazone of the aldehyde isomeric with the ketone was not detected.

3,3-Dimethylhexanol-2. To 14 g of magnesium turnings covered with absolute ether was added a solution of 94 g of dimethylpropylbromomethane (b.p. 51.5-53° at 44-46 mm) in an equal volume of ether. Upon completion of addition of the bromide over a period of 2-3 hours, an ethereal solution of 26 g of acetaldehyde was introduced into the reaction mixture. On the following day the reaction products were decomposed with ice water, acidified with sulfuric acid, and extracted with ether. The extract was dried with fused potash. The yield was 10.9 g (14.7%) of dimethyl-3,3-hexanol-2.

B. p. 85-86.5° (28 mm), d_0^0 0.8809, d_{20}^{20} 0.8472, d_4^{20} 0.8459, n_D^{20} 1.4353, MR_D 40.19; Calculated 40.67.

Found %: C 73.69, 73.85; H 13.99, 14.04. M 135, 139. $C_8H_{18}O$. Calculated %: C 73.78; H 13.93. M 130.

Preparation of 3,3-dimethylhexanone-2 by oxidation of this alcohol was not successful.

3,3-Dimethylhexanone-2. By treating with excess acetic acid-semicarbazide the combined intermediate fractions from the products of the reaction of 3,3-dimethylhexyne-1 with acetic, propionic, and butyric acids, there was obtained 14 g of the semicarbazone of 3,3-dimethylhexanone-2 with m.p. 121-123°. To this was added 150 ml of 13% H_2SO_4. The reaction mixture was heated to boiling, the reaction products were steam distilled off, and the water lost was replenished from a dropping funnel to maintain a constant concentration of sulfuric acid. The upper layer of the distillate contained the ketone, which was separated, washed with sodium carbonate solution, and dried with calcium chloride. The yield of crude product was 6.7 g (70%). The 3,3-dimethylhexanone-2 did not react with an ammoniacal solution of silver oxide and gave a positive iodoform reaction.

B.p. 151-152°, d_0^0 0.8413, d_{20}^{20} 0.8269, d_4^{20} 0.8257, n_D^{20} 1.4175, MR_D 39.09; calculated 39.16. Found %: C 74.94, 74.93, H 12.37, 12.62. $C_8H_{16}O$. Calculated %: C 74.94; H 12.57.

The boiling point of the ketone prepared by us agreed with the data in the literature [4].

The semicarbazone of 3,3-dimethylhexanone-2 prepared in the usual way [2], after recrystallization from alcohol and drying at 70° to constant weight, melted at 121-122°.

The melting point of the semicarbazone of 3,3-dimethylhexanone-2 obtained by dehydration of 2,3-dimethylhexanediol-2,3 was 119-120° [4].

Found %: N 22.74, 22.68. $C_9H_{19}ON_3$. Calculated %: N 22.68.

SUMMARY

1. Three vinyl β-esters have been synthesized and described for the first time: 2-acetoxy-3,3-dimethylhexene-1; 2-propionoxy-3,3-dimethylhexene-1; and 2-butyroxy-3,3-dimethylhexene-1.

2. Hydrolysis in the presence of acetic acid-semicarbazide was employed to determine the position of the acyloxy groups in the molecules of the vinyl β-esters.

3. Among the starting, intermediate, and by-products of the synthesis of the esters of 3,3-dimethylhexen-1-ol-2 that were prepared and described for the first time were 3,3-dimethylhexanol-2; 1,1-dichloro-3,3-dimethylhexane; 1-chloro-3,3-dimethylhexene-1; and 3,3-dimethylhexyne-1.

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THE MECHANISM OF DEHYDRATION OF γ-GLYCOLS

III. STUDY OF THE DEHYDRATION OF 2-CYCLOHEXYL-2,5-PENTANEDIOL AND 1,4-PENTANEDIOL

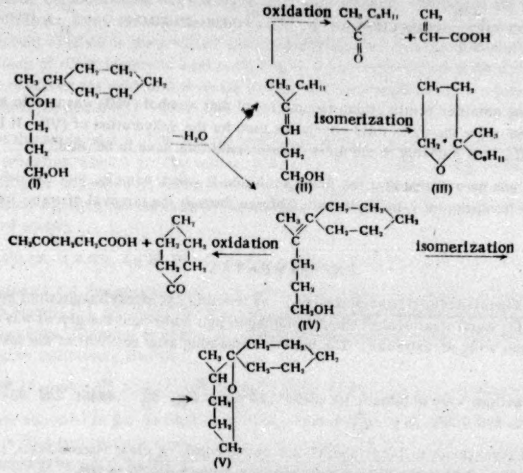
T. A. Favorskaya, O. V. Sergievskaya and N. P. Ryzhova

We had shown [1, 2] that primary-tertiary γ-glycols with aliphatic radicals, the same as the ditertiary γ-glycol-2,5-dimethyl-2,5-hexanediol, form as the first product of dehydration the corresponding unsaturated β-ethylenic alcohols, which readily isomerize into tetrahydrofuran derivatives. The corresponding glycol with an aromatic radical–2-phenyl-2,5-pentanediol– does not form an unsaturated alcohol on dehydration, and instead is directly converted into 2,2-methyl-phenyltetrahydrofuran by the cleavage of water from the two hydroxyl groups of the glycol.

2-Phenyl-2-penten-5-ol, obtained by a different method, failed to isomerize into the tetrahydrofuran derivative under the usually studied conditions, and was converted into it only under fairly drastic conditions, where its hydration to yield the glycol was possible, which then cleaved water from the two hydroxyl groups.

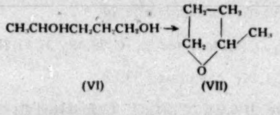
We explained the inability of 2-phenyl-2-penten-5-ol to isomerize into the tetrahydrofuran derivative as being due to the presence of a conjugated system of double bonds in it. To confirm this postulation we decided to study the dehydration of a glycol containing the cyclohexyl radical, and specifically, 2-cyclohexyl-2,5-pentanediol. This glycol was synthesized by us by the reaction of either cyclohexylmagnesium chloride or bromide with acetopropyl alcohol. On distillation with sulfuric acid (pH 1.6) the glycol simultaneously gave two products – an unsaturated alcohol and a cyclic compound. When distilled with traces of sulfuric acid the isolated unsaturated alcohol isomerized into the cyclic compound. To prove its structure the unsaturated alcohol was oxidized with permanganate; the neutral products obtained here represented a mixture of methyl cyclohexyl ketone and cyclohexanone. Such oxidation results indicated that the dehydration of 2-cyclohexyl-2,5-pentanediol proceeds in two possible directions with the formation of two unsaturated alcohols: 2-cyclohexyl-2-penten-5-ol and 2-cyclohexylidene-5-pentanol. The result of oxidizing a mixture of these alcohols should give in the first case – methyl cyclohexyl ketone and hydracrylic acid, the latter easily undergoing transformation into acrylic acid, and in the second case – cyclohexanone and levulinic acid. Our postulation that the dehydration of the glycol proceeded in such a manner was confirmed by the analysis of the silver salts of the obtained acids. Both unsaturated alcohols are easily isomerized into the corresponding pyran and furan derivatives.

The obtained mixture of cyclic derivatives was subjected to oxidation; the obtained lactones were converted into the silver salts of hydroxy acids of composition $C_{11}H_{20}O_3$. An acid of such composition could have been obtained from both lactone (III) and lactone (V), and this makes it impossible to decide the structure of the obtained lactone and thus answer the question of whether both possible isomers were formed or whether only one lactone was obtained.



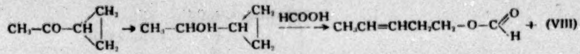
All of the glycols studied by us contained tertiary alcohol groups in their composition; it was interesting to learn how a glycol, containing a secondary alcohol group instead of the tertiary group, would dehydrate. For this we studied the dehydration of the secondary-primary γ-glycol – 1,4-pentanediol (VI), obtained by the reduction of acetopropyl alcohol with 3% sodium amalgam. We studied the dehydration of the glycol under extremely varied conditions: treatment with sulfuric acid, formic acid, and potassium acid sulfate. The concentration of the aqueous sulfuric acid solutions was varied within broad limits: 0.12, 5, 7, 10 and 20%. In addition to the aqueous solutions we also took a 7% alcoholic H_2SO_4 solution, while the formic acid was taken as 10 and 15%.

The experiments were run in the cold, at 50°, at the temperature of the boiling water bath and with distillation, and in not a single instance were we able to isolate the unsaturated alcohol – 3-penten-1-ol (VIII), but instead we always obtained either recovered starting glycol, or 2-methyltetrahydrofuran, or a mixture of these two compounds.



The absence of the unsaturated alcohol $CH_3CH = CHCH_2CH_2OH$ (VIII) in the dehydration products led us to believe that the dehydration of (VI) proceeds as the result of the removal of water from the two hydroxyls of the glycol. However, on the other hand, it could be postulated that (VIII) is formed, but that it shows such rapid isomerization that its isolation from the reaction products is impossible.

To verify the last postulation, we prepared alcohol (VIII) by a different method. The reduction of acetyltrimethylene gave methyl-cyclopropylcarbinol, which when heated with formic acid (1 : 1) gave a mixture of (VIII) and its formic ester. Hydrolysis of thi[illegible]e with 20% potash solution gave 3-penten-1-ol (VIII), which proved to be stable, and when distilled with seve[illegible]ops of sulfuric acid it failed to isomerize into 2-methyltetrahydrofuran (VII).



On the basis of the obtained results it can be concluded that alcohol (VIII) was unable to isomerize into 2-methyltetrahydrofuran under the quite mild conditions used for the dehydration of (VI). If it is at all capable of isomerizing into (VII), then probably much more drastic conditions have to be used.

Consequently, it can be assumed that the first postulation is valid, namely, that the dehydration of glycol (VI) leads to the direct formation of 2-methyltetrahydrofuran through the removal of water from the two hydroxyl groups.

EXPERIMENTAL

2-Cyclohexyl-2,5-pentanediol (I) was synthesized by reacting cyclohexylmagnesium bromide with acetopropyl alcohol. After the usual treatment of the organomagnesium compound the glycol was extracted with ether, both manually and using an extractor. The product remaining after removal of the solvent was vacuum-distilled.

The following fractions were obtained: 1st 40-90° (14 mm), 4 g, n_D^{20} 1.4646; 2nd 95-100° (14 mm), 2.8 g, n_D^{20} 1.4757; 3rd 168-169°, 13 g, n_D^{20} 1.4909.

The last fraction corresponds to 2-cyclohexyl-2,5-pentanediol. A clear viscous mass, it begins to crystallize on long standing. The yield in the different experiments range from 23 to 26%.

d_4^{20} 0.9966, n_D^{20} 1.4909, MR_D 54.10; calculated 53.85.

Found %: C 71.22; H 11.68, active H 1.97. $C_{11}H_{22}O_2$. Calculated %: C 70.91; H 11.90; active H 2.0.

Repeated redistillation of the low-boiling fractions finally gave 3.5 g of substance with b.p. 93-95.5° (9 mm), which decolorized $KMnO_4$ and contained traces of hydroxyl.

n_D^{20} 1.4768, d_4^{20} 0.9215, M 163.9. $C_{12}H_{22}$. Calculated: M 166.

Judging from the constants [3], molecular weight and analysis, this substance represents bicyclohexyl with unreacted acetopropyl alcohol, the presence of which was shown in the lower boiling fraction, as impurity.

Transformation of 2-Cyclohexyl-2,5-pentanediol (I). Glycol (I) was steam-distilled from sulfuric acid solution (pH 1.6). The concentration of the solution was maintained constant by the addition of water. The distilled product, rapidly decolorizing $KMnO_4$ solution, was extracted with ether, the extract dried over K_2CO_3, and the ether distilled. Distillation of the residue gave two products: 1) b.p. 95-98° (13 mm); yield 19-30%, and 2) b.p. 124° (12 mm); yield 20-26%.

1) d_4^{20} 0.9380, n_D^{20} 1.4711, MR_D 50.07; calculated 50.24.

Found %: C 78.56; H 11.84. $C_{11}H_{20}O$. Calculated %: C 78.49; H 11.88.

2) d_4^{20} 0.9374, n_D^{20} 1.4830, MR_D 51.14; calculated 51.88.

Found %: C 78.10; H 12.24; active H 0.95. $C_{11}H_{20}O$. Calculated %: C 78.49; H 11.88; active H 1.

The first product is either oxide (III) or (V), and the second is either unsaturated alcohol (II) or (IV).

When heated with a drop of concentrated sulfuric acid the alcohol (n_D^{20} 1.4859) was isomerized into the oxide with b.p. 97-100° (13 mm) and n_D^{20} 1.4736. Here a part of the alcohol was converted into tar.

The alcohol (2.2 g) was oxidized with 6.9 g of $KMnO_4$. After filtration and washing with hot water the MnO_2 precipitate was boiled with ether for 2 hours. The small amount of neutral product isolated from this extract gave a semicarbazone with m.p. 171° (from alcohol); the semicarbazone of methyl cyclohexyl ketone melts at 171-172° [4]. Steam-distillation of the water solution of oxidation products gave neutral products, which with 2,4-dinitrophenylhydrazine gave a copious yellow precipitate with m.p. 158.5° (from alcohol with the addition of ethyl acetate). The mixed melting point of the obtained hydrazone with the 2,4-dinitrophenylhydrazone of authentic cyclohexanone was not depressed. The solution, obtained in the oxidation of the salts, was acidified with sulfuric acid; the organic acids that separated here were converted into the silver salts, which from the amount of silver in them (52.67 and 52.98%) indicated that the obtained acids were a mixture of acids. The amount of silver in acrylic acid is 63.51%, in hydracrylic acid it is 54.82%, and in levulinic acid it is 48.43%. The results of the oxidation revealed that the alcohol obtained by us represented a mixture of the two isomeric alcohols (II) and (IV).

Oxidation of the oxide with b.p. 95-98° (13 mm) was continued for 7 days; the total amount of $KMnO_4$ consumed for the oxidation was 3.5 g. The solitary product of the oxidation was a crystalline product with m.p. 55-56°, showing neutral reaction, which makes it necessary to assume that it is the lactone of the hydroxy acid with composition $C_{11}H_{20}O_3$ (on the basis of the analysis of the silver salt obtained from it, crystallizing with 6 molecules of water).

Found %: C 32.12; H 4.93; Ag 26.28. $C_{11}H_{19}O_3Ag \cdot 6H_2O$. Calculated %: C 31.80; H 7.47; Ag 26.02.

Transformation of 1,4-Pentanediol (VI). The primary-secondary γ-glycol – 1,4-pentanediol – was obtained by the Lipp method [5], involving the reduction of acetopropyl alcohol with 3% sodium amalgam. The maximum yield was 60%. Attempts to obtain the glycol in good yield by other methods indicated in the literature [6] failed to give satisfactory results.

B.p. 98.5-99° (1 mm), d_4^{20} 0.9903, n_D^{20} 1.4461, MR_D 28.11. $C_5H_{12}O_2$. Calculated 28.31.

The distillate obtained in the distillation of 15 g of 1,4-pentanediol with 20% sulfuric acid was saturated with potash and the obtained products were extracted with ether; the extract after drying and removal of the solvent by distillation gave 4.2 g (34.5%) of 2-methyltetrahydrofuran.

B. p. 77-78°, d_4^{20} 0.8485, n_D^{20} 1.4040, MR_D 24.91. $C_5H_{10}O$. Calculated: 24.61. Literature [5]: b.p. 77-78°.

3-Penten-1-ol (VIII). The methylcyclopropylcarbinol needed for the synthesis of 3-penten-1-ol was obtained by the Demyanov method [7], involving the reduction of 17 g of acetyltrimethylene with sodium alcoholate. The yield of alcohol was 7.2 g (40%).

B.p. 119-120°, d_4^{20} 0.8901, n_D^{20} 1.4254.

A mixture of 27 g of methylcyclopropylcarbinol and 70 ml of formic acid (1 : 1) was heated at the boil for 1 hour. After neutralization of the acid with soda the reaction products were extracted with ether, the ether was distilled from the dried extract, and the residue was distilled at atmospheric pressure. The following fractions were obtained: 1st b.p. 119-122°, 1.3 g; 2nd b.p. 125-130°, 11.2 g and 3rd b.p. 130-135°, 3.5 g.

The 1st fraction contained recovered methylcyclopropylcarbinol; the 2nd and 3rd fractions were a mixture of 3-penten-1-ol and its formic ester. Both fractions were hydrolyzed with 20% K_2CO_3 solution. The heating and stirring was continued for 11 hours. Distillation of the obtained products gave two fractions: 1st, b.p. 125-135°, 5.1 g – a mixture of the alcohol and its ester; and 2nd, b.p. 135-137°, 2 g (23%) – 3-penten-1-ol:

d_4^{20} 0.8597, n_D^{20} 1.4338, MR_D 26.04. $C_5H_{10}O\digamma$. Calculated 26.35.

Literature [8]: b.p. 136-137°, n_D^{20} 1.4343, 1.4339.

The 3-penten-1-ol (1.5 g) was distilled with a drop of concentrated sulfuric acid. The alcohol was recovered unchanged, and isomerization into the tetrahydrofuran derivative failed to occur.

SUMMARY

1. 2-Cyclohexyl-2,5-pentanediol was synthesized and its reaction with sulfuric acid was studied.

2. It was established that the dehydration proceeds in two possible directions with the formation of two alcohols – 2-cyclohexyl-2-penten-5-ol and 2-cyclohexylidene-5-pentanol.

3. When vacuum-distilled with traces of acid the unsaturated alcohols are isomerized into a cyclic compound, giving on oxidation the lactone of a hydroxy acid.

4. The dehydration of 2-cyclohexyl-2,5-pentanediol proceeds by the mechanism proposed earlier for the dehydration of primary-tertiary γ-glycols.

5. The dehydration of the primary-secondary γ-glycol – 1,4-pentanediol – was studied under the influence of various acid solutions of variable concentration and it was shown that the solitary dehydration product is 2-methyltetrahydrofuran.

6. It was shown that under the influence of dilute formic acid methylcyclopropylcarbinol isomerized into the primary alcohol 3-penten-1-ol, which when distilled with sulfuric acid fails to isomerize into the tetrahydrofuran derivative.

7. It was postulated that the dehydration of 1,4-pentanediol does not proceed through the intermediate formation of the unsaturated alcohol 3-penten-1-ol, but instead proceeds through the direct removal of water from the two hydroxyl groups of the glycol.

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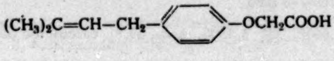
CONDENSATION OF METHYLETHYLVINYLCARBINOL WITH PHENOL IN THE PRESENCE OF PHOSPHORIC ACID

A. I. Kakhniashvili and T. N. Kiparenko

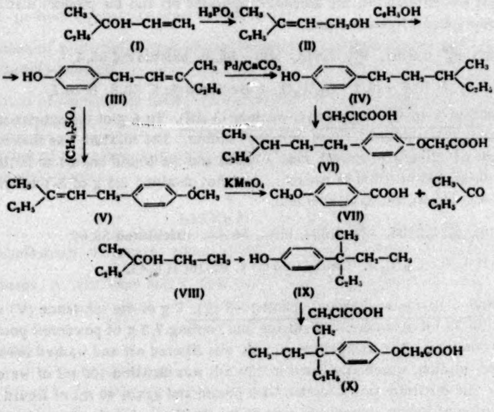
One of us was able to condense phenol with dimethylvinylcarbinol in the presence of phosphoric acid and ascarite [1]. It was shown that condensation of phenol with dimethylvinylcarbinol was accompanied by isomerization of the tertiary carbinol into the primary with the formation of a para-substituted phenol from it.

As the work of I. N. Nazarov, A. Azerbaev and V. Pakcheeva [2] has shown, with an increase in the weight of the alkyl radicals the isomerization rate of dialkylvinylcarbinols decreases. It was interesting to discover what effect an increase in the weight of the alkyl radicals would have on the condensation reaction of methylethylvinylcarbinol with phenol. It should also be noted that phenoxycarboxylic acids are widely used as stimulators in plant growth, and unsaturated homologs of phenoxycarboxylic acids may be more active than saturated ones.

Investigations on 2-methyl-4-(p-carboxymethoxyphenyl-butene-2



showed that a 0.01% solution of this compound accelerates the blooming of buds of grafts.



Methylethylvinylcarbinol (I) condensed with phenol under the effect of phosphoric acid less vigorously than did dimethylvinylcarbinol. This gave a para-substituted phenol-3-methyl-5-(p-hydroxyphenyl)-pentene-3 (III), corresponding to the primary alcohol (II) – 3-methyl-penten-2-ol-1. On hydrogenation in the presence of Pd on calcium carbonate, the para-substituted phenol absorbed 1 molecule of hydrogen and was converted into 3-methyl-5-(p-hydroxyphenyl)-pentane (IV). Methylation of the unsaturated para-substituted phenol (III) with dimethylsulfate gave its methyl ether (V) and oxidation of the latter gave anisic acid (VII) and methyl ethyl ketone. In the reaction of the saturated para-substituted phenol (IV) with chloroacetic acid, the corresponding crystalline 3-methyl-5-(carboxymethoxyphenyl)-pentane (VI) was obtained.

For comparison, we also condensed phenol with methyldiethylcarbinol (VIII). The condensation of the saturated carbinol with phenol under the effect of phosphoric acid proceeded with considerably more difficulty than that of methylethylvinylcarbinol. Condensation of methyldiethylcarbinol with phenol gave 3-methyl-3-(p-hydroxyphenyl)-pentane (IX), which reacted with chloroacetic acid to give crystalline 3-methyl-3-(p-carboxymethoxyphenyl)-pentane (X).

EXPERIMENTAL

Methylethylvinylcarbinol was prepared by hydrogenating methylethylacetylenylcarbinol in the presence of Pd on calcium carbonate. It had b.p. 114-115°, n_D^{20} 1.4265 [2].

Condensation of methylethylvinylcarbinol with phenol in the presence of phosphoric acid. 16 g of methylethylvinylcarbinol was added dropwise at room temperature (18°) with continuous stirring to a mixture of 11 g of phenol and 12 g of phosphoric acid (d 1.700). The reaction proceeded with the evolution of heat and towards the end of the addition of the carbinol the temperature of the mixture reached 24°. After addition of the carbinol, stirring was continued for a further 3 hours at 40-45°. The reaction mixture was diluted with ether and washed with water and then several times with a 10% solution of caustic soda. The alkaline extracts were combined, acidified with dilute hydrochloric acid and extracted with ether, the ether solution was dried with sodium sulfate and after distilling off the ether, the residue was distilled in vacuum. We thus isolated 9 g of 3-methyl-5-(p-hydroxyphenyl)-pentene-3 (III).

B.p. 140-143° (7 mm), d_4^{20} 1.0016, n_D^{20} 1.5375, MR_D 54.9; calculated 55.0.

Found %: C 82.0, 82.1; H 9.4, 9.4. $C_{12}H_{16}O$. Calculated %: C 81.8; H 9.1.

Hydrogenation of 3-methyl-5-(p-hydroxyphenyl)-pentene-3 (III). On hydrogenating 3 g of the substance in 25 ml of ethyl alcohol in the presence of 0.4 g of Pd on calcium carbonate 440 ml of hydrogen (20°, 742 mm) was taken up. The catalyst was filtered off, the alcohol evaporated off and the product distilled. We obtained 2 g of 3-methyl-5-(p-hydroxyphenyl)-pentane (IV).

B.p. 144-145° (8 mm), d_4^{20} 0.9691, n_D^{20} 1.513, MR_D 55.5; calculated 55.4.

Found %: C 81.1, 80.8; H 10.5, 10.4. $C_{12}H_{18}O$. Calculated %: C 80.8; H 10.1.

Methylation of 3-methyl-5-(p-hydroxyphenyl)-pentene-3 (III). To 6 g of the substance dissolved in 30 ml of 10% caustic soda solution was added 6 ml of dimethyl sulfate. The mixture was shaken for half an hour. Then the solution was made alkaline with caustic soda solution and the liquid heated to boiling. The product was extracted with ether, dried and distilled in vacuum. We thus obtained 2.5 g of 3-methyl-5-(p-methoxyphenyl)-pentene-3 (V) as a colorless, transparent liquid.

B.p. 138-140° (6 mm), d_4^{20} 0.9903, n_D^{20} 1.534, MR_D 59.44; calculated 59.69.

Found %: C 82.05; H 9.39. $C_{13}H_{18}O$. Calculated %: C 82.10; H 9.47.

Oxidation of 3-methyl-5-(p-methoxyphenyl)-pentene-3 (V). 2 g of the substance (V) was added to a solution of 0.5 g of potash in 70 ml of water; with stirring and cooling 7.7 g of powdered potassium permanganate was added to the mixture obtained. The manganese dioxide was filtered off and washed several times with hot water. From the combined solution, which amounted to 150 ml, was distilled 100 ml of water together with the volatile neutral products. The distillate was saturated with potash and again 40 ml of liquid was distilled off. On adding an aqueous solution of iodine and caustic soda to the distillate, a voluminous precipitate of iodoform was produced (methyl ethyl ketone). After distilling off the neutral products, the residue was evaporated to small volume and acidified with hydrochloric acid when crystals with m.p. 180-181° (from water) were precipitated. These did not depress the melting point of p-methoxybenzoic acid.

Condensation of 3-methyl-5-(p-hydroxyphenyl)-pentane (IV) with chloroacetic acid. 1 g of the substance (IV) was dissolved in 10 ml of 10% caustic soda solution, 1.5 g of chloroacetic acid added and the mixture heated on a boiling water bath for 1.5 hours. Then the liquid was acidified and extracted with ether, the ether solution was washed with dilute soda solution and the alkaline extract obtained was acidified with dilute hydrochloric acid. The 3-methyl-5-(p-carboxymethoxyphenyl)-pentane (VI) isolated had m.p. 98-99° (from aqueous alcohol).

Found %: C 70.80; H 8.50. M (neutr.) 235. $C_{14}H_{20}O_3$. Calculated %: C 71.18; H 8.54. M 236.

Condensation of phenol with methyldiethylcarbinol in the presence of phosphoric acid. 20 g of methyldiethylcarbinol (VIII) was added dropwise with continuous stirring at the temperature of a boiling water bath to a mixture of 13 g of phenol and 12 ml of phosphoric acid (d 1.704). After addition of the carbinol, stirring was continued for a further 40 hours at the temperature of a boiling water bath. The reaction mixture was then worked up as in the previous experiment. We isolated 10 g of 3-methyl-3-(p-hydroxyphenyl)-pentane (IX) as a colorless, oily liquid.

B.p. 145-150° (5 mm), d_4^{18} 0.979, n_D^{18} 1.535, MR_D 55.74; calculated 55.40.

Found %: C 80.35; H 9.58. $C_{12}H_{18}O$. Calculated %: C 80.80; H 10.10.

Condensation of 3-methyl-3-(p-hydroxyphenyl)-pentane (IX) with chloroacetic acid was carried out under the same conditions as in the condensation of (IV); the acid obtained (X) – 3-methyl-3-(p-carboxymethoxyphenyl)-pentane had m.p. 134° (from aqueous alcohol).

Found %: C 70.70; H 8.73. M 227.3. $C_{14}H_{20}O_3$. Calculated %: C 71.18; H 8.54. M 236.

SUMMARY

1. Condensation of phenol with methylethylvinylcarbinol in the presence of phosphoric acid gave 3-methyl-5-(p-hydroxyphenyl)-pentene-3, corresponding to the primary alcohol 3-methyl-penten-2-ol-1.

2. Methylation of 3-methyl-5-(p-hydroxyphenyl)-pentene-3 with dimethylsulfate gave 3-methyl-5-(p-methoxyphenyl)-pentene-3, and oxidation of the latter gave anisic acid and methyl ethyl ketone.

3. 1 Molecule of hydrogen was absorbed in the hydrogenation of 3-methyl-5-(p-hydroxyphenyl)-pentene-3 and 3-methyl-5-(p-hydroxyphenyl)-pentane was formed.

4. Condensation of 3-methyl-5-(p-hydroxyphenyl)-pentane with chloroacetic acid gave 3-methyl-5-(p-carboxymethoxyphenyl)-pentane.

5. Condensation of phenol with methyldiethylcarbinol in the presence of phosphoric acid gave 3-methyl-3-(p-hydroxyphenyl)-pentane.

6. Condensation of 3-methyl-3-(p-hydroxyphenyl)-pentane with chloroacetic acid gave 3-methyl-3-(p-carboxymethoxyphenyl)-pentane.

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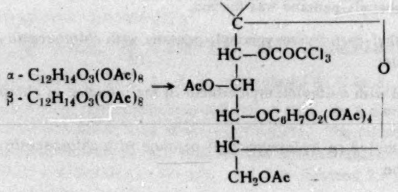
THE EFFECT OF PHOSPHORUS PENTACHLORIDE ON OCTAACETYLCELLOBIOSE AND THE ANOMERIC SUGAR ACETATES•

S. N. Danilov, O. P. Kozmina and A. N. Shirshova

For the purpose of synthesizing α-cellobiosan (1,2-anhydrocellobiose) by Brigl's method [1], we investigated the effect of phosphorus pentachloride on the α- and β-octaacetates of cellobiose and, for comparison, on the α- and β-pentaacetates of D-glucose. By treating D-glucose β-pentaacetate [2] and maltose β-octaacetate [3] with phosphorus pentachloride, Brigl substituted a chlorine for the acetyl group of the first carbon atom and chlorinated the acetyl of the second carbon atom to the trichloroacetyl group (in the case of maltose, two anomeric tetrachlorides were obtained). But he did not suceed in carrying out this reaction with cellobiose octaacetate. Brigl supposed that sugar α-acetates did not react with phosphorus pentachloride with the formation of tetrachlorinated derivatives. The reaction of the α- and β-pentaacetates of glucose with phosphorus pentachloride gave tetrachloro substituted derivatives, with the difference that in the case of glucose β-pentaacetate one product was obtained – 1-chloro-2-trichloroacetyl-3,4,6-triacetyl-D-glucose – while according to our experiments the α-pentaacetate of D-glucose gave at first a low melting mixture, and the above tetrachloride was obtained from it by crystallization. Probably, the α-pentaacetate of D-glucose gives a mixture of tetrachloride stereoisomers, which differ in stability. Brigl also obtained two anomeric chlorides by treating maltose octaacetate with phosphorus pentachloride. Cellobiose octaacetate (m.p. 229.5°, $[\alpha]^{20}_{D}$ + 42.0°), synthesized by acetolysis of cellulose and usually considered as the α-form and octaacetylcellobiose (m.p. 192°, $[\alpha]^{20}_{D}$ — 14.5°), referred to as the β-form [4], form the same 1-chloro-2-trichloroacetylhexaacetylcellobiose, characterized by us.



α - $C_{12}H_{14}O_3(OAc)_8$
β - $C_{12}H_{14}O_3(OAc)_8$
H Cl
C
HC—OCOCCl$_3$
O
AcO—CH
HC—OC$_6$H$_7$O$_2$(OAc)$_4$
HC
CH$_2$OAc

However, the lower melting isomer – β-octaacetylcellobiose – gave a smaller yield of the above tetrachloride than the higher melting α-octaacetate of cellobiose, as, apparently, the β-octaacetate gave not one, but a mixture of two stereoisomeric α- and β-tetrachlorides.

The experimental data we obtained justifies the following hypotheses.

1) Brigl's conclusion that β-anomeric, but not α-anomeric, sugar acetates react with phosphorus pentachloride should be corrected as actually this reaction does occur for the α- and β-forms but with different yields of the more stable tetrachloride.

• This article is Report IV in the series "Anhydrides, amino- and guanido-derivatives of carbohydrates and polyatomic alcohols." See J. Gen. Chem., 25, 2106 (1955) for Report III.

2) The nomenclature of the α- and β-anomeric forms of sugars should be further refined as some discrepancies are noticeable in the properties of the main examples of sugars, in particular, the vagueness in the behavior of the α- and β-forms with phosphorus pentachloride. The standard definition of the α- and β-forms of sugars according to the relation [5] of the values of their angles of rotation of the polarization plane does not guarantee that the α-forms do, actually, always correspond to the cis-position (as in α-D-glucose) and the β-forms – to the trans-position (as in β-D-glucose) of the hydroxyl groups at the first and at the second carbon atom. Usually, but not always, the melting point of the β-forms of the D-series is higher, while the $[\alpha]^{20}_{D}$ is lower than those of the α-forms. However, the α-octaacetate of cellobiose has a higher melting point and $[\alpha]^{20}_{D}$ than does the β-octaacetate. The clarification of this problem appears interesting when investigating α-cellobiosan and α-maltosan that have not yet been described. It is not clear whether the α-octaacetate rather than the β-octaacetate of cellobiose is actually formed by the acetolysis of cellulose.

In accordance with the standard definitions of α- and β-forms of cellobiose octaacetates, one of us [6] had supposed earlier that in the acetolysis, alcoholysis and hydrolysis of cellulose molecule chains, by the addition of acetic anhydride, alcohol and water at the 1 and 4 carbon atoms, such forms are produced which have hydroxyl and OR-groups at the 1 and 4 carbon atoms on one side of the pyranose ring and are α-forms.

However, it might be expected that acetolysis of cellulose with a break in the bridging β-glucose bonds would give β-octaacetate of cellulose, if one assumes that no Walden inversion occurs, such as usually accompanies the formation and breaking of ethylene oxide rings in a monose [7]. Thus, the acetyl groups are placed directly at the free valencies of the cellobiose bi-radical, formed as an intermediate in the acetolysis of cellobiose.

A thorough investigation of α-anhydrides of sugars, as well as the acetolysis and hydrolysis of polysaccharides and the reactions of phosphorus pentachloride with anomeric sugar acetates would help to clarify the structures and properties of α- and β-anomeric forms.

The problem as to which of the anomeric structures of cellobiose and maltose, as well as of their octaacetates, are α(cis)- and which are β(trans)-forms should be considered an open question.

EXPERIMENTAL

Treatment of cellobiose α-octaacetate with phosphorus pentachloride. Into a flask fitted with a condenser and a stirrer were placed 34 g of cellobiose octaacetate, prepared by the acetolysis of cotton cellulose [4] (m.p. 220° and $[\alpha]^{20}_{D}$ + 42.1°), 52.5 g of phosphorus pentachloride and 40 ml (5 moles) of freshly distilled tetrachloroethane.

As the starting materials were heated, they dissolved in the tetrachloroethane and began to react at 85 – 90° with the evolution of hydrogen chloride. With an increase in temperature the reaction speeded up. As decomposition began above 120°, the temperature in the reaction flask was kept at 100-105°. After 4 hours bubbles of gas separated very slowly. By this time only half of the octaacetate had reacted. In order to get the bulk of the octaacetate to react under the given conditions, heating was continued for 10 hours. To eliminate the possibility of moisture entering the apparatus and to absorb the hydrogen chloride evolved, the condenser was connected to a drier and a solution of soda. At the end of the reaction we obtained a transparent yellow solution and, after distilling off the solvent and phosphorus compounds in vacuum, this yielded a low melting substance, which solidified on cooling to give a uniform, transparent, friable, amber-yellow mass.

To remove the rest of the phosphorus compounds, the substance was dissolved in chloroform and the solution washed with ice-water till neutral and dried. After distilling off the solvent we obtained a low melting crystalline product, which was freed from traces of the original octaacetate by dissolving in ether, fractional precipitation from the ether solution with petroleum ether and recrystallization. We obtained about 20 g of chloride and isolated 3.7 g of unreacted cellobiose octaacetate. The substance was recrystallized several times from a mixture of ethyl ether and petroleum ether until it showed a constant angle of rotation of the plane of polarization. The finely crystalline powder, m.p. 80° (not sharp), was readily soluble in chloroform, ethyl ether, benzene, alcohol and carbon tetrachloride, with much difficulty in ligroin and almost insoluble in petroleum ether. It gradually dissolved in Fehling's solution with weak reduction, apparently as the substituents were hydrolyzed. For 1-chloro-2-trichloroacetyl-hexaacetylcellobiose (0.3552 g of substance in 10 ml of chloroform, l 0.95 dm) we found $[\alpha]^{20}_{D}$ + 28.2°.

Found %: C 41.14; H 4.63; Cl 18.54. M 732 (cryoscopy in C_6H_6). $C_{26}H_{32}O_{17}Cl_4$. Calculated %: C 41.17; H 4.25; Cl 18.71. M 758.

The structure of the substance was confirmed by various reactions, for example hydrolysis.

0.5512 g of substance; 0.2352 g NaOH (5.88 ml of 1 N solution). $C_{26}H_{32}O_{17}Cl_4$ (containing 8 acidic groups). Calculated 0.2326 g NaOH.

The readily hydrolyzable chlorine was determined by acid hydrolysis: the substance was heated in 50% acetic acid solution in the presence of 0.25 g of sodium acetate for 1.5 hours on a water bath and the HCl evolved was precipitated with a solution of $AgNO_3$.

Found %: Cl 4.79. at 1 atm. Cl in $C_{26}H_{32}O_{17}Cl_4$ calculated 4.68% Cl.

The latter experiments show that three quarters of the total amount of chlorine in the molecule of the chloride obtained is held quite stably, while at the same time one atom of chlorine is readily hydrolyzed.

The distinctive isonitrile smell on heating the substance in a solution of potassium hydroxide in methyl alcohol with aniline indicates the presence of a trichloroacetyl group in the molecule.

The formation of trichloroacetamide, isolated on hydrolyzing the chloride, serves as a direct proof of the presence of a trichloroacetyl group. For this 5.00 g of the substance was dissolved in 25 ml of methyl alcohol, saturated with ammonia at 0° and kept at room temperature for 24 hours. After evaporating off the alcohol and the ammonia in vacuum, a semisolid mass remained, which, on exhaustive extraction with ether, was converted into a powder that kept well in the absence of moisture and deliquesced in air.

From the ether extract we obtained two products, which we were able to separate as a result of their different solubilities in cold water. The part of the product which was readily soluble in water, as was expected, was acetamide. The part of the product, which was insoluble in cold water (containing a large amount of chlorine) dissolved in hot water and on cooling precipitated as needle-like crystals.

After two recrystallizations from water and from chloroform, the product had m.p. 141°, which corresponded to the melting point of trichloroacetamide. A mixed melting point with an authentic preparation of trichloroacetamide was not depressed. The ether insoluble part of the hydrolysis product dissolved readily in water, rotated the plane of polarization and with phenylhydrazine gave an osazone with m.p. 203°, corresponding to the osazone of cellobiose.

Thus it may be considered proved that we prepared 1-monochloro-2-trichloroacetyl-hexaacetyl cellobiose.

Treatment of cellobiose β-octaacetate with phosphorus pentachloride. A mixture of 15.4 g of phosphorus pentachloride, 10 ml of tetrachloroethane and 10 g of cellobiose β-octaacetate (m.p. 191° and $[\alpha]_D^{20}$ −14°), prepared by acetylating cellobiose in the presence of anhydrous sodium acetate, was heated at 100-102°. The reaction proceeded noticeably more quickly than with the higher melting cellobiose α-octaacetate, and was complete after 2.5 hours.

As a result of purification from traces of the original octaacetate and several crystallizations we isolated about 3 g of a substance with $[\alpha]_D^{20}$ + 28.0°, which was completely identical with the hexaacetyl cellobiose tetrachloride, prepared from cellobiose α-octaacetate. Both substances melted at 80° and a mixed melting point was not depressed.

Found %: C 41.21; H 4.48; Cl 18.50. $C_{26}H_{32}O_{17}Cl_4$. Calculated %: C 41.17; H 4.25; Cl 18.71.

On boiling with aniline in an alcoholic alkali solution the typical isonitrile smell appeared.

Treatment of glucose α-pentaacetate with phosphorus pentachloride. The reaction was carried out under the conditions used by Brigl for β-pentaacetyl glucose [2]. 19.5 g of freshly prepared glucose α-pentaacetate (m.p. 110° and $[\alpha]_D^{20}$ + 101.3°) was mixed with 52 g of PCl_5 and the mixture heated without solvent on a water bath. The substances reacted vigorously with the evolution of hydrogen chloride. As a result we obtained a mixture of two chlorides (with a total ester content of 30%), one of the components of which was higher melting and separated more readily than the other, as needle-like crystals.

After several recrystallizations from a mixture of ether and petroleum ether we obtained a substance with m.p. 140° and reached a constant rotation of the plane of polarization of $[\alpha]_D^{18}$ + 3.4°.

Found %: Cl 30.09. $C_{14}H_{16}O_9Cl_4$. Calculated %: Cl 30.17.

According to analysis data and properties, the substance was completely identical with the tetraacetyl glucose chloride prepared by Brigl on treating glucose β-pentaacetate with phosphorus pentachloride. This was also confirmed by the absence of depression in a mixed melting point with Brigl's chloride, which we prepared from glucose β-pentaacetate.

SUMMARY

1. Treatment of both anomeric α- and β-octaacetates of cellobiose with phosphorus pentachloride gave the same product – 1-monochloro-2-trichloroacetyl-hexaacetylcellobiose.

2. When treated with phosphorus pentachloride, the α-pentaacetate of D-glucose apparently gave a mixture of two tetrachlorides, but only one tetraacetylglucose tetrachloride could be isolated from the mixture in a crystalline state and this had been obtained by Brigl from D-glucose β-pentaacetate.

Thus, in contradiction to Brigl's statement, the reaction with phosphorus pentachloride occurs with α- and β-anomers of monoses and disaccharides.

3. The discrepancies in the relations of melting points and angles of rotation of α- and β-octaacetates of cellobiose to those of α- and β-pentaacetates of D-glucose make the principle by which anomeric compounds are defined problematic as well as the reference of cis- and trans-configurations for α- and β-anomers, respectively.

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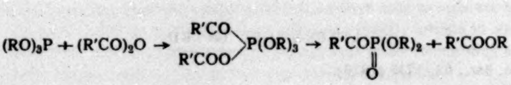
THE EFFECT OF ANHYDRIDES OF ORGANIC ACIDS ON TRIALKYL PHOSPHITES AND SODIUM DIALKYL PHOSPHITES

Gilm Kamai and V. A. Kukhtin

When treated with alkyl halides the full esters of phosphorous acids are converted into esters of phosphinic acids by the Arbuzov rearrangement [1]. As was shown by M. I. Kabachnik and P. A. Rossiiskaya [2], acid halides also affect trialkyl phosphites in an analogous way.

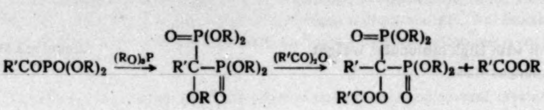
Investigations carried out by us show that acid anhydrides are also capable of reacting with trialkyl phosphites in an analogous way. Treatment of full esters of phosphorous acid with the anhydrides of acetic, butyric and benzoic acids gave the corresponding esters of α-ketophosphinic acid and the ester of the organic acid. These reactions probably proceed by a scheme analogous to Arbuzov rearrangement.



$$(RO)_3P + (R'CO)_2O \rightarrow \begin{matrix}R'CO\\ R'COO\end{matrix}\!\!>P(OR)_3 \rightarrow R'CO\underset{\underset{\displaystyle O}{\|}}{P}(OR)_2 + R'COOR$$

The acid anhydrides, as could be expected, were less active in this reaction than acid chlorides. A high temperature was required for the reaction.

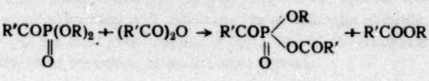
Besides the esters of α-ketophosphinic acids, in some cases a product, with a higher boiling point and the same elementary composition but double the molecular weight, was obtained in large amounts. An analogous product was obtained by A. E. Arbuzov and M. M. Azanovskaya [3] on treating sodium diethyl phosphite with acetyl chloride. We put forward and checked experimentally a scheme for the formation of the dimeric product, analogous to A. E. Arbuzov and M. M. Azanovskaya's scheme,



$$R'COPO(OR)_2 \xrightarrow{(RO)_3P} R'\overset{\overset{\displaystyle O{=}P(OR)_2}{|}}{\underset{\underset{\displaystyle OR}{|}}{C}}{-}\underset{\underset{\displaystyle O}{\|}}{P}(OR)_2 \xrightarrow{(R'CO)_2O} R'{-}\overset{\overset{\displaystyle O{=}P(OR)_2}{|}}{\underset{\underset{\displaystyle R'COO}{|}}{C}}{-}\underset{\underset{\displaystyle O}{\|}}{P}(OR)_2 + R'COOR$$

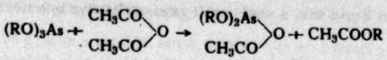
By heating a mixture of triethyl phosphite and the ethyl ester of acetylphosphinic acid we obtained an addition product corresponding to the first state of the reaction. When treated with acetic anhydride it gave a dimeric product and ethyl acetate.

In some cases a third product was also detected in the reaction products. It had an active carbonyl group and, according to the analytical data, was a mixed anhydride of alkoxy-α-ketophosphinic acid and an organic acid. Its formation could proceed by the following scheme:



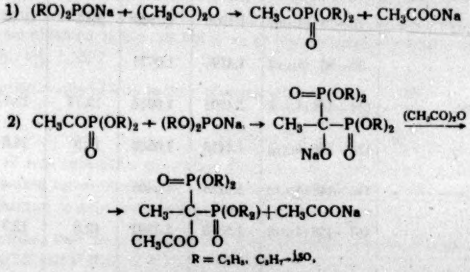
$$R'CO\underset{\underset{\displaystyle O}{\|}}{P}(OR)_2 + (R'CO)_2O \rightarrow R'CO\underset{\underset{\displaystyle O}{\|}}{P}\!\!<\begin{matrix}OR\\ OCOR'\end{matrix} + R'COOR$$

It is interesting to note that, as established by one of us together with Khisamov [4], acid anhydrides react with the esters of arsenous acid in this way only to give a mixed anhydride.



$$(RO)_3As + \begin{matrix}CH_3CO\\ CH_3CO\end{matrix}\!>O \rightarrow \begin{matrix}(RO)_2As\\ CH_3CO\end{matrix}\!>O + CH_3COOR$$

Furthermore, we investigated the effect of acetic anhydride on sodium dialkyl phosphite. Similarily to an acid chloride, acetic anhydride reacts with sodium dialkyl phosphite at room temperature in an ether solution. As in the experiments of A. E. Arbuzov and M. M. Azanovskaya, as a result of the reaction a dimeric product was formed which did not have an active carbonyl group. The course of this reaction may be explained by the following scheme:



$$1)\ (RO)_2PONa + (CH_3CO)_2O \rightarrow CH_3CO\underset{\underset{O}{\|}}{P}(OR)_2 + CH_3COONa$$

$$2)\ CH_3CO\underset{\underset{O}{\|}}{P}(OR)_2 + (RO)_2PONa \rightarrow CH_3-\overset{\overset{O=P(OR)_2}{|}}{\underset{\underset{NaO}{|}}{C}}-\underset{\underset{O}{\|}}{P}(OR)_2 \xrightarrow{(CH_3CO)_2O}$$

$$\rightarrow CH_3-\overset{\overset{O=P(OR)_2}{|}}{\underset{\underset{CH_3COO}{|}}{C}}-\underset{\underset{O}{\|}}{P}(OR_2) + CH_3COONa$$

$$R = C_2H_5,\ C_3H_7\text{-iso}.$$

The first stage of the second part of the reaction was checked experimentally by A. E. Arbuzov and M. M. Azanovskaya. The second stage requires checking experimentally.

The results obtained by us show that not only various halide derivatives, but also compounds, not containing active halide, in particular acid anhydrides, may participate in the Michaelis-Becker reaction [5]. The constants of compounds obtained by us are given in the table.

EXPERIMENTAL*

Reaction of acetic anhydride and triethyl phosphite. 33.2 g of triethyl phosphite and 20.4 g of acetic anhydride were heated in an Arbuzov flask, set up for vacuum distillation, for 6 hours at 120-140°. During this time, 12.8 g (72.7%) of ethyl acetate distilled over. On distilling the reaction products, two products were isolated: 1) b.p. 84-86° (44 mm), n_D^{20} 1.4126, d_0^{20} 1.0979. This was a transparent, colorless liquid (3.9 g), almost without smell. It gave an intense color with sodium nitroprusside. With dinitrophenylhydrazine it formed yellow needle-like crystals with m.p. 152-153°. It gave a characteristic color with Schiff's reagent. The constants of the compound obtained are identical with those described earlier by M. I. Kabachnik and P. A. Rossiiskaya for the ethyl ester of acetylphosphinic acid.

2) B. p. 156-157° (2 mm), n_D^{20} 1.4325, d_0^{20} 1.1579. The substance obtained (11.8 g) did not give qualitative reactions for an active carbonyl group. The constants are identical with those described earlier by A. E. Arbuzov and M. M. Azanovskaya for the dimeric product. Acetic anhydride reacted similarly with triisobutyl phosphite.

Reaction of acetic anhydride with trimethyl phosphite. 10 g of trimethyl phosphite and 7 g of acetic anhydride were heated for 6 hours at 110-120°. During the reaction time 3.1 g of methyl acetate distilled over. As a result of two distillations the methyl ester of acetylphosphinic acid was isolated.

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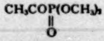
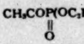
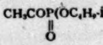
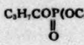
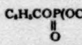
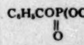
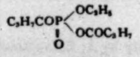
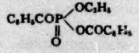
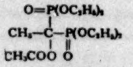
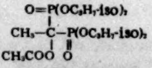
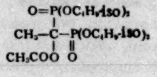
* The authors would like to thank V. Pavlova and A. Kuklina, who participated in the experimental part of the work.

B.p. 78-79° (4 mm), n_D^{20} 1.4206, d_0^{20} 1.2109, MR_D 31.83; calculated 32.54.

Found %: P 19.80. $C_4H_9O_4P$. Calculated %: P 19.89.

The colorless, transparent liquid with a weak smell gave qualitative reactions for an active carbonyl group.

Trimethyl phosphite reacted similarly with benzoic anhydride.

Sample No.	Formula	Boiling point	n_D^{20}	d_0^{20}	P (in %)	
					calculated	found
1	 $CH_3CO\underset{\underset{O}{\|}}{P}(OCH_3)_2$	78—79 (4mm)	1.4206	1:2109	20.4	19.8
2	 $CH_3CO\underset{\underset{O}{\|}}{P}(OC_2H_5)_2$	84—86 (4mm)	1.4196	1.0976	—	—
3	 $CH_3CO\underset{\underset{O}{\|}}{P}(OC_4H_9\text{-iso})_2$	144—146 (4mm)	1.4305	1.0018	13.17	12.71
4	 $C_3H_7CO\underset{\underset{O}{\|}}{P}(OC_2H_5)_2$	124—126 (4mm)	1.4418	1.0580	14.9	14.8
5	 $C_6H_5CO\underset{\underset{O}{\|}}{P}(OCH_3)_2$	146—148 (4mm)	1.5254	1.2405	—	—
6	 $C_6H_5CO\underset{\underset{O}{\|}}{P}(OC_2H_5)_2$	157—158 (4mm)	1.5050	1.1591	12.8	12.7
7	 $C_3H_7CO\underset{\underset{O}{\|}}{P}\Big\langle\begin{matrix}OC_2H_5\\OCOC_3H_7\end{matrix}$	143—145 (2mm)	1.4385	1.0547	12.2	12.4
8	 $C_6H_5CO\underset{\underset{O}{\|}}{P}\Big\langle\begin{matrix}OC_2H_5\\OCOC_6H_5\end{matrix}$	194—196 (3mm)	1.5168	1.1401	9.64	9.54
9	 $CH_3-\overset{\overset{O=P(OC_2H_5)_2}{\vert}}{\underset{\underset{CH_3COO}{\vert}}{C}}-\underset{\underset{O}{\|}}{P}(OC_2H_5)_2$	156—157 (2mm)	1.4325	1.1579	—	—
10	 $CH_3-\overset{\overset{O=P(OC_3H_7\text{-iso})_2}{\vert}}{\underset{\underset{CH_3COO}{\vert}}{C}}-\underset{\underset{O}{\|}}{P}(OC_3H_7\text{-iso})_2$	159—162 (3mm)	1.4312	1.0823	—	—
11	 $CH_3-\overset{\overset{O=P(OC_4H_9\text{-iso})_2}{\vert}}{\underset{\underset{CH_3COO}{\vert}}{C}}-\underset{\underset{O}{\|}}{P}(OC_4H_9\text{-iso})_2$	174—178 (2mm)	1.4375	1.0481	13.17	12.8

Reaction of butyric anhydride with triethyl phosphite. 20 g of triethyl phosphite and 19 g of butyric anhydride were heated for 8 hours at 150°; as a result, 7.1 g of ethyl butyrate distilled over (b.p. 120°, n_D^{20} 1.3948, d_0^{20} 0.878). As a result of distilling the reaction products we obtained two fractions. 1) The ethyl ester of butyrylphosphinic acid.

B.p. 124-125° (4 mm), d_0^{20} 1.0580, n_D^{20} 1.4418, MR_D 50.08; calculated 51.00.

Found %: P 14.79. M 208. $C_8H_{17}O_4P$. Calculated %: P 14.91, M 218.

The colorless, transparent liquid (4.5 g) gave qualitative reactions with sodium nitroprusside and Schiff's reagent.

2) The ethyl ester of butyrylphosphinic butyric anhydride.

B.p. 143-145° (4 mm), d_0^{20} 1.0547, n_D^{20} 1.4365, MR_D 59.27; calculated 61.20.

Found %: P 12.4 M 257. $C_{10}H_{19}O_5P$. Calculated %: P 12.2. M 250.

The colorless liquid (5 g) with a specific smell, had an active carbonyl group, did not dissolve in water but dissolved in acetone, alcohol and benzene. The reaction between triethyl phosphite and benzoic anhydride proceeded in the same way.

Reaction of acetic anhydride with sodium diethyl phosphite. Sodium diethyl phosphite was prepared by adding 20 g of diethyl phosphorous acid to 3.5 g of sodium wire in absolute ether. 15.5 g of acetic anhydride was added to the solution of sodium diethyl phosphite obtained. As the anhydride was added, a precipitate of sodium acetate formed and the temperature rose to 26-30°.

After the addition of all the anhydride, the reaction mixture was heated for 30 minutes on a water bath. After cooling, the precipitate was filtered off on a vacuum filter and the ether was distilled off. As a result of vacuum distillation we obtained 12.6 g (50.7%) of α,α-tetraethyldiphosphorous ethyl acetate. B.p. 157° (3 mm), d_0^{20} 1.4318, n_D^{20} 1.1597.

A similar reaction occurred with sodium diisopropyl phosphite.

SUMMARY

1. The effect of acid anhydrides on trialkyl phosphites was investigated. It was established that trialkyl phosphites react with acid anhydrides to give esters of α-ketophosphinic acids. A scheme for this reaction, which is analogous in mechanism to Arbuzov rearrangement, was put forward.

2. It was established that the side products of these reactions are mixed anhydrides of alkoxy-α-ketophosphinic and organic acids and a dimeric product, which does not have an active carbonyl group.

3. It was established that acid anhydrides are capable of reacting with sodium dialkyl phosphite, as are acid chlorides.

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* Original Russian pagination. See C.B. Translation.

THE EFFECT OF CARBON TETRACHLORIDE ON MIXED ALKYL ESTERS OF PHOSPHOROUS ACID

Gilm Kamai and F. M. Kharrasova

One of us had shown earlier [1] that carbon tetrachloride is not a passive solvent of alkyl esters of phosphorous acid, but reacts with them analogously to alkyl halides, according to the well known scheme. Further work [2] showed that alkyl esters of arylphosphinic, diarylphosphinic, pyrophosphinic and subphosphinic acids, i. e., all esters containing a trivalent phosphorous atom, react with carbon tetrachloride relatively easily.

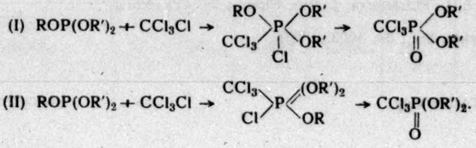
As a continuation and development of our previous investigations, this work is aimed at examining the reactions of certain mixed alkyl esters of phosphorous acid with carbon tetrachloride.

The starting mixed trialkyl phosphites were synthesized by reacting monoalkyl phosphorous acid chlorides with alcohols in the presence of bases.

$$ROPCl_2 + 2R'OH + 2C_6H_5N(CH_3)_2 \rightarrow ROP(OR')_2 + 2C_6H_5N(CH_3)_2 \cdot HCl.$$

The mixed trialkyl phosphites obtained by us were mobile liquids with characteristic smell. These esters, as derivatives of trivalent phosphorous, are very reactive compounds. They oxidize in air, react with copper monochloride with the evolution of heat and add sulfur readily with the formation of the corresponding esters of thiophosphoric acid.

Mixed alkyl esters of phosphorous acid, react with carbon tetrachloride, when gently heated, to form mixed or unmixed alkyl esters of trichloromethylphosphinic acid by the schemes:

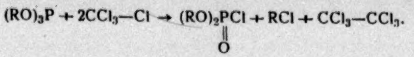


$$\text{(I)}\quad ROP(OR')_2 + CCl_3Cl \rightarrow \begin{matrix}RO\\CCl_3\end{matrix}{>}\underset{\underset{Cl}{|}}{P}{<}\begin{matrix}OR'\\OR'\end{matrix} \rightarrow CCl_3\underset{\underset{O}{\|}}{P}{<}\begin{matrix}OR'\\OR'\end{matrix}$$

$$\text{(II)}\quad ROP(OR')_2 + CCl_3Cl \rightarrow \begin{matrix}CCl_3\\Cl\end{matrix}{>}P{<}\begin{matrix}(OR')_2\\OR\end{matrix} \rightarrow CCl_3\underset{\underset{O}{\|}}{P}(OR')_2.$$

As a rule with this reaction, the lighter radical of the phosphite separates in the form of the alkyl chloride.

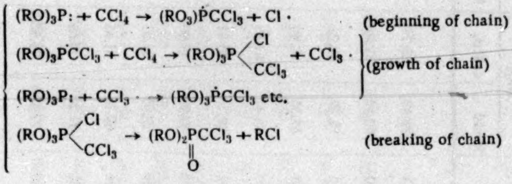
As a result of the experiments, we synthesized some alkyl esters of trichloromethylphosphinic acid. The esters isolated by us were colorless liquids with a characteristic fruitlike smell, which distilled, without decomposition, under vacuum. The ester yields were in most cases less than 50%. Such a low yield of esters of trichloromethylphosphinic acid may be explained, firstly, by the facile capacity of the mixed esters of phosphorous acid to rearrange their radicals and their tendency towards symmetrization, and secondly, by the presence of side reactions which result in the formation of acid chlorides and hexachloroethane by the scheme put forward previously by one of us [3].



$$(RO)_3P + 2CCl_3{-}Cl \rightarrow (RO)_2\underset{\substack{\|\\ O}}{P}Cl + RCl + CCl_3{-}CCl_3.$$

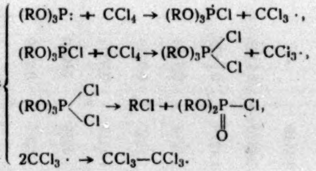
On the basis of considerable experimental material, one could conclude that the reaction of alkyl esters of trivalent phosphorous acids with carbon tetrachloride proceeded by a chain mechanism. If one assumes that the initiator of the beginning of the chain is the lone pair of phosphorous electrons of the trialkyl phosphite, then the most probable reaction mechanism may be expressed by schemes 1 and 2.

1st Scheme



$$\begin{cases} (RO)_3P{:} + CCl_4 \rightarrow (RO_3)\dot{P}CCl_3 + Cl\cdot & \text{(beginning of chain)} \\ (RO)_3\dot{P}CCl_3 + CCl_4 \rightarrow (RO)_3P\begin{smallmatrix} Cl \\ CCl_3 \end{smallmatrix} + CCl_3\cdot & \text{(growth of chain)} \\ (RO)_3P{:} + CCl_3\cdot \rightarrow (RO)_3\dot{P}CCl_3 \text{ etc.} & \\ (RO)_3P\begin{smallmatrix} Cl \\ CCl_3 \end{smallmatrix} \rightarrow (RO)_2\underset{\substack{\|\\ O}}{P}CCl_3 + RCl & \text{(breaking of chain)} \end{cases}$$

2nd Scheme



$$\begin{cases} (RO)_3P{:} + CCl_4 \rightarrow (RO)_3\dot{P}Cl + CCl_3\cdot, \\ (RO)_3\dot{P}Cl + CCl_4 \rightarrow (RO)_3P\begin{smallmatrix} Cl \\ Cl \end{smallmatrix} + CCl_3\cdot, \\ (RO)_3P\begin{smallmatrix} Cl \\ Cl \end{smallmatrix} \rightarrow RCl + (RO)_2\underset{\substack{\|\\ O}}{P}{-}Cl, \\ 2CCl_3\cdot \rightarrow CCl_3{-}CCl_3. \end{cases}$$

By hydrolysis of the methyl n-butyl, ethyl n-butyl and n-butyl isobutyl esters of trichloromethylphosphinic acid in a sealed tube with a 15% solution of hydrochloric acid at 145-150°, we isolated trichloromethylphosphinic acid with m.p. 85-86°, indentical to the preparation first isolated by A. Ya. Yakubovich and V. A. Ginsburg [4].

The first experiment by G. Kamai and L. P. Egorova [1] on the hydrolysis of alkyl esters of trichloromethylphosphinic acid were carried out under more drastic conditions and were therefore unsuccessful. It should be noted, however, that G. Kamai and Z. L. Khisamova [5] were the first to obtain trichloromethyl-p-tolylphosphinic acid by hydrolyzing the ethyl ester of trichloromethyl-p-tolylphosphinic acid and to study its derivatives.

EXPERIMENTAL

The starting acid chlorides of ethyl and n-butyl phosphorous acids were prepared by the usual method [6].

Preparation of dimethyl ethyl phosphite. A solution of 40 g of ethyl phosphorous chloride in 40 ml of ethyl ether was added from a dropping funnel with continuous stirring and external cooling to an ether solution of 20 g of methyl alcohol and 68 g of dimethylaniline at such a rate that the reaction temperature did not rise above 5-10°. Then the contents of the flask were stirred for a further hour at 30-35°. The precipitated crystals of dimethylaniline hydrochloride were filtered off, pressed out and washed with ether. The ether was distilled off from the filtrate and the residual liquid was distilled in vacuum. After a series of distillations we obtained dimethyl ethyl phosphite as a colorless, mobile liquid.

B.p. 28-29° (14 mm), 122-124° (759 mm), d_4^{20} 1.0259, n_D^{20} 1.4110, MR_D 33.43; calculated 33.74.

Found %: P 22.61, 22.40. $C_4H_{11}O_3P$. Calculated %: P 22.47.

TABLE 1

Physical Properties of Mixed Trialkyl Phosphites

Sample No.	Formula	Boiling point at given pressure (mm)	n_D^{20}	d_0^0	d_4^{20}	MR_D		P content (in %)	
						found	calcd.	found	calcd.
1	$C_2H_5OP(OCH_3)_2$*	28—30° (14)	1.4110	—	1.0259	33.43	33.74	22.40	22.47
2	$C_2H_5OP(OC_3H_7)_2$-iso *	65.5—66.5 (18)	1.4150	0.9471	0.9280	52.40	52.21	15.64	15.95
3	$C_2H_5OP(OC_3H_7)_2$-n	85—87 (17)	1.4215	0.9720	0.9519	51.79	52.21	15.80	15.95
4	$C_2H_5OP(OC_4H_9)_2$-iso	86—89 (5)	1.4258	0.9462	0.9266	61.36	61.45	14.14	13.94
5	$C_2H_5OP(OC_4H_9)_2$-n	120.5—122 (10)	1.4285	0.9510	0.9330	61.41	61.45	13.70	13.94
6	$C_2H_5OP(OC_5H_{11})_2$-iso	110—112 (10)	1.4315	0.9311	0.9152	70.75	70.61	12.45	12.35
7	$C_4H_9OP(OCH_3)_2$	65—66 (18)	1.4215	1.0010	0.9822	42.91	43.00	18.35	18.65
8	$C_4H_9OP(OC_2H_5)_2$	72—74 (13)	1.4262	0.9749	0.9560	52.05	52.21	16.09	15.96
9	$C_4H_9OP(OC_3H_7)_2$-iso	76—78 (10)	1.4170	0.9405	0.9196	60.78	61.45	14.12	14.10
10	$C_4H_9OP(OC_4H_9)_2$-iso	91—92 (5)	1.4283	—	0.9050	71.20	70.69	12.82	12.40
11	$C_4H_9OP(OC_5H_{11})_2$-iso	114—114.5 (4)	1.4350	0.9303	0.9151	79.38	79.62	11.61	11.15

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* Literature data [7] for: 1) b.p. 124-127°, 2) b.p. 69-71° (10 mm).

TABLE 2

Physical Properties of Thiophosphates

Sample No.	Formula	Boiling point at given pressure (mm)	n_D^{20}	d_0^0	d_4^{20}	MR_D		P content (in %)		Yield (in %)
						found	calcd.*	found	calcd.	
1	$C_2H_5O\underset{\substack{\| \\ S}}{P}(OCH_3)_2$	79.5—80.5° (17)	1.4530	1.1891	1.1634	39.59	40.09	18.01	18.21	88.3
2	$C_2H_5O\underset{\substack{\| \\ S}}{P}(OC_3H_7)_2$-iso	106—108 (23)	1.4425	1.0376	1.0176	58.89	58.59	13.72	13.70	85.0
3	$C_2H_5O\underset{\substack{\| \\ S}}{P}(OC_3H_7)_2$-n	105—107 (13)	1.4475	1.0579	1.0388	58.25	58.59	14.45	13.70	83.3
4	$C_2H_5O\underset{\substack{\| \\ S}}{P}(OC_4H_9)_2$-iso	134—135 (16)	1.4450	1.0116	0.9942	68.09	67.84	12.23	12.18	75.5
5	$C_2H_5O\underset{\substack{\| \\ S}}{P}(OC_4H_9)_2$-n	135—137 (13)	1.4486	1.0146	0.9969	68.39	67.84	12.70	12.18	81.3
6	$C_2H_5O\underset{\substack{\| \\ S}}{P}(OC_5H_{11})_2$-iso	127—129 (5)	1.4530	1.0054	0.9881	77.28	77.04	11.04	10.97	88.7
7	$C_4H_9O\underset{\substack{\| \\ S}}{P}(OCH_3)_2$	100—102 (13)	1.4545	1.1342	1.1144	48.22	49.37	16.21	15.62	31.0
8	$C_4H_9O\underset{\substack{\| \\ S}}{P}(OC_2H_5)_2$	116—117 (14)	1.4502	1.0540	1.0354	58.75	58.60	13.65	13.67	77.1
9	$C_4H_9O\underset{\substack{\| \\ S}}{P}(OC_5H_{11})_2$ iso	126—127 (9)	1.4544	0.9860	0.9695	85.77	86.88	9.71	9.98	50.6

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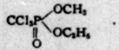
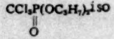
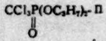
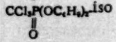
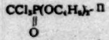
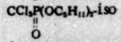
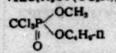
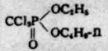
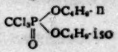
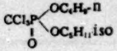
* AR_D for P was taken as 3.75.

** The thiophosphates prepared, which are reported in the table, were colorless liquids with unpleasant smell.

TABLE 3

Properties of the Alkyl Esters of Trichloromethylphosphinic acid

Sample No.	Formula	Boiling point at given pressure (mm)	n_D^{20}	d_0^0	d_4^{20}	MR_D found	MR_D calc.	P content (in %) found	P content (in %) calc.	Yield (in %)
1	 $CCl_3\underset{\overset{\|}{O}}{P}\genfrac{}{}{0pt}{}{OCH_3}{OC_2H_5}$	116—118° (10)	1.4620	1.4602	1.4368	46.59	46.14	12.82	12.85	60.1
2	 $CCl_3\underset{\overset{\|}{O}}{P}(OC_3H_7)_2$-iso	95 (4)	1.4560	1.3094	1.2883	59.83	60.00	10.82	10.95	94.9
3	 $CCl_3\underset{\overset{\|}{O}}{P}(OC_3H_7)_2$-n	123—125 (7)	1.4625	1.3310	1.3098	59.57	60.00	11.21	10.95	35.6
4	 $CCl_3\underset{\overset{\|}{O}}{P}(OC_4H_9)_2$-iso	141—143 (10)	1.4585	1.2604	1.2406	68.65	69.23	10.23	9.96	70.0
5	 $CCl_3\underset{\overset{\|}{O}}{P}(OC_4H_9)_2$-n	150—153 (10)	1.4600	1.2690	1.2454	68.52	69.23	10.12	9.96	45.2
6	 $CCl_3\underset{\overset{\|}{O}}{P}(OC_5H_{11})_2$-iso									
	via $C_2H_5OP(OC_5H_{11})_2$-iso	133—135 (3)	1.4615	1.2204	1.2016	77.64	78.47	10.45	9.15	45.1
	via $C_4H_9OP(OC_5H_{11})_2$-iso	163—164 (10)	1.4590	1.1920	1.1728	79.17	78.47	9.39	9.15	35.0
7	 $CCl_3\underset{\overset{\|}{O}}{P}\genfrac{}{}{0pt}{}{OCH_3}{OC_4H_9\text{-n}}$	125—126 (7)	1.4625	1.3476	1.3264	55.91	55.38	11.31	11.51	30.8
8	 $CCl_3\underset{\overset{\|}{O}}{P}\genfrac{}{}{0pt}{}{OC_2H_5}{OC_4H_9\text{-n}}$	105—107 (5)	1.4602	1.3351	1.3180	58.93	59.01	11.28	10.89	44.5
9	 $CCl_3\underset{\overset{\|}{O}}{P}\genfrac{}{}{0pt}{}{OC_4H_9\text{-n}}{OC_4H_9\text{-iso}}$	105—109 (3)	1.4545	1.2715	1.2528	64.38	64.61	10.51	10.41	50.1
10	 $CCl_3\underset{\overset{\mid}{O}}{P}\genfrac{}{}{0pt}{}{OC_4H_9\text{-n}}{OC_5H_{11}\text{iso}}$	150—151 (11)	1.4575	1. —	1.2084	70.29	69.23	10.21	9.96	83.6

In a similar way, i. e. by reacting the acid chlorides of alkyl phosphorous acids with alcohols in the medium of ether and a base, we prepared the other mixed esters of phosphorous acid (except the esters 8 and 10). The data on the esters obtained are given in Table 1.

Preparation of diethyl n-butyl phosphite. A mixture of 37 g of n-butyl alcohol and 60.5 g of dimethylaniline was added to 68.5 g of phosphorous trichloride in 700 ml of absolute ether with continuous stirring and external cooling of the flask in snow. Then a mixture of 46 g of ethyl alcohol and 121.2 g of dimethylaniline was added from the same dropping funnel to the mass obtained. Then the mixture was heated on a water bath for 1 hour. After filtering off the dimethylaniline hydrochloride and distilling off the ethyl ether, the residual liquid was fractionally distilled in vacuum. The diethyl n-butyl phosphite isolated was a colorless liquid.

B.p. 72-74° (13 mm), d_0^0 0.9749, d_4^{20} 0.9561, n_D^{20} 1.4262, MR_D 52.05; calculated 52.21.

Found %: P 16.09, 16.04. $C_8H_{19}O_3P$. Calculated %: P 15.96.

In the same way we synthesized diisoamyl n-butyl phosphite.

The mixed trialkyl phosphites-1,2 were synthesized previously by Landayer and Rydon [7], but they cited only their boiling points. The yields of the esters varied from 30 to 69%.

Preparation of dimethyl ethyl thiophosphate. Into a flask was placed 5.52 g of dimethyl ethyl phosphite and 10 ml of absolute ether and to this was added 1.28 g of sulfur. The addition reaction proceeded with the evolution of heat. To complete the reaction, the flask was heated under reflux for 1 hour. In a subsequent distillation, the reaction product distilled at 79.5-80.5° (17 mm). The yield was 6.1 g (88.3%). The freshly distilled dimethyl ethyl thiophosphate was a colorless liquid with an unpleasant smell.

d_0^0 1.1841, d_4^{20} 1.1631, n_D^{20} 1.4530, MR_D 39.53; calculated 40.03.

Found %: P 18.11. $C_4H_{11}O_3SP$. Calculated %: P 18.21.

The other thiophosphates were synthesized in a similar way and their constants are given in Table 2.

Preparation of the methyl ethyl ester of trichloromethylphosphinic acid. Into a flask with a reflux condenser was placed 9 g of ethyl dimethyl phosphite and 10.4 g of carbon tetrachloride. The flask was heated on an oil bath for 4 hours. After cooling, the flask was weighed and the loss in weight was 3.9 g (theoretical 3.1 g). The residual liquid was distilled in vacuum. The methyl ethyl ester of trichloromethylphosphinic acid was a colorless liquid with a fruity smell.

B.p. 116-118° (10 mm), n_D^{20} 1.4670, d_0^0 1.4602, d_4^{20} 1.4381, MR_D 46.59; calculated 46.14.

Found %: P 12.82, 12.68. $C_4H_8Cl_3O_3P$. Calculated %: P 12.85.

The preparation of the other esters of trichloromethylphosphinic acid was by the method given above, i.e. heating equimolecular amounts of the appropriate phosphite and carbon tetrachloride. The data on the esters synthesized are given in Table 3.

Hydrolysis of the methyl n-butyl ester of trichloromethylphosphinic acid. 1.6 g of the methyl n-butyl ester of trichloromethylphosphinic acid and 12 ml of a 15% hydrogen chloride solution were heated in a sealed tube at 145-150° for 4 hours. After cooling, the tube was opened when a high pressure was found to have been produced. Then the contents of the tube, which consisted of two layers, were separated. After evaporating off the methyl chloride from the upper oily layer, a liquid remained with n_D^{18} 1.4040, which corresponded to almost pure n-butyl chloride. After evaporation in vacuum, the lower aqueous part yielded 1.35 g of a crystalline mass with m.p. 77-79°. After recrystallization from a mixture of ether and benzine and then 10 hours drying over phosphorous pentoxide, the crystalline material melted at 85-86° and according to the phosphorous analysis, corresponded to trichloromethylphosphinic acid described previously [4].

Experiments on the hydrolysis of the ethyl n-butyl and isobutyl n-butyl esters of trichloromethylphosphinic acid proceeded similarly to that described above.

SUMMARY

1. By reacting acid chlorides of ethyl and n-butyl phosphorous acids with various alcohols in the presence of dimethylaniline or pyridine, new examples of mixed alkyl esters of phosphorous acid were obtained and investigated.

2. The mixed trialkylphosphites isolated as derivatives of trivalent phosphorus, react with copper monochloride and add sulfur readily to form trialkyl thiophosphates.

3. It was established that on treating the corresponding mixed esters of phosphorus acid with carbon tetrachloride various mixed and unmixed esters of trichloromethylphosphinic acid were formed with the elimination of the lighter radical of the phosphite in the form of the alkyl chloride.

4. Hydrolysis of esters of trichloromethylphosphinic acid with dilute hydrochloric acid gave trichloromethylphosphinic acid as the monohydrate.

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PREPARATION OF AROMATIC PRINCIPLES OF THE TERPENOCYCLOHEXANOL AND TERPENOCYCLOHEXANONE SERIES

V. N. Belov and L. A. Heifitz

In the last few years reports have appeared on the use of terpenophenols for the preparation of aromatic principles [1-5]. Considering that this trend in the synthesis of aromatic principles has good prospects, we introduced a menthyl or bornyl radical into the phenol molecule by the alkylation of phenols with menthyl chloride and a mixture of bornyl and isobornyl chlorides. The menthyl chloride was prepared by reacting menthol with phosphorus pentachloride in a benzene solution [6]; phosphorus pentachloride reacted with borneol to give a mixture of bornyl chloride and its stereoisomer isobornyl chloride (m.p. 122-125°) with a predominance of the latter. However, in alkylating with a mixture of these chlorides at a relatively high temperature with hydrogen chloride and a solvent, whatever the phenol used, the isobornyl chloride, which is an exo-isomer, is practically totally converted into the more stable endo-isomer – bornyl chloride – and bornylphenols are the only reaction products. Menthyl chloride has been used to alkylate phenol; the mixture of bornyl and isobornyl chlorides has been used for the alkylation of phenol, o-cresol and m-cresol. Condensation was achieved by boiling the chloride for a long time with an excess of the appropriate phenol and resulted in the formation of the corresponding terpenophenols, and not isomeric arylterpenic ethers;* as has been shown by N. I. Kursanov [6], the hydrogen chloride evolved during the reaction acted as a catalyst. On the basis of one paper [6], one can maintain that in the condensation of menthyl chloride with phenol, the main reaction product is p-menthylphenol and, furthermore, the hydroxyphenyl group has a tertiary position at the C_4 in the menthyl radical. In the case of bornylphenols in the formulas given below, we assume, conditionally, a para-position for the bornyl radical and consider that the hydroxyaryl radical in the bornylphenols has the same position as the hydroxyl group in borneol. The terpenophenols, prepared by us in 66-87% yields, were very viscous, yellowish tarlike substances with a weak characteristic smell. They dissolved in organic solvents. They did not steam distil or dissolve even in a large excess of 10% solutions of caustic alkali, which made it easy to separate them from other phenols with no noticeable losses. The terpenophenols in themselves, are uninteresting as aromatic principles; the pleasant smell, judging from the data available [1-5], appears only after hydrogenation of the aromatic nucleus and the conversion of terpenophenols into the corresponding terpenocyclohexanols. We carried out the hydrogenation in the presence of Raney nickel; it proceeded very smoothly at 112-180° and a pressure of 145-170 atm. with the absorption of the calculated amount of hydrogen. The yield of terpenocyclohexanols was 70-85.5%. The alcohols obtained have not been described in the literature; they are extremely viscous, colorless liquids, which remain unchanged after long storage.

Except for menthylcyclohexanol, none of the bornylcyclohexanols form crystalline derivatives – phenylurethans, α-naphthylurethans, as well as 3,5-dinitrobenzoates and their derivatives with α-naphthylamine.

Menthylcyclohexanol has a very weak cedarlike smell; the alcohols, containing a bornyl radical, have a stronger smell. Bornylcyclohexanol, itself, has a weak but very stable, slight cedarlike smell. On changing to bornyl-3-methylcyclohexanol the character of the smell does not change but becomes weaker, while it becomes stronger in bornyl-2-methylcyclohexanol which is due, apparently, to the presence of a tertiary carbon atom, attached to a methyl, next to the alcohol group. Furthermore, the bornyl-2-methylcyclohexanol smell acquires a slight sandalwood nuance.

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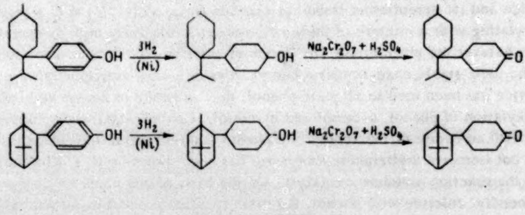
* The amount of arylterpenic ethers formed was established in each case by determining the hydroxyl group content of the condensation product and was 2-3% in the condensation of menthyl chloride with phenol, and was ~4-5, 7-8 and 15-18% in the condensation of a mixture of bornyl and isobornyl chlorides with m-cresol, phenol and o-cresol, respectively.

As the acetates of some alicyclic alcohols have a finer and stronger smell than the alcohols themselves [7, 8], we acetylated the terpenocyclohexanols obtained with acetic anhydride in the presence of phosphoric acid [9]. The acetates obtained were colorless liquids, considerably less viscous than the original alcohols, and, contrary to expectations, almost without smell.

We used chromic acid to oxidize the terpenocyclohexanols to the corresponding ketones. The yield of ketones was 51.5-80.8%; they have not been described previously in the literature.

The change to ketones, as could be expected, resulted in a considerable increase in smell; terpenocyclohexanones, containing a bornyl radical, have a pleasant smell and only menthylcyclohexanone has an unpleasant, persistent smell. Bornylcyclohexanone has a fine and stable smell, reminiscent of the smell of ionone preparations on the one hand, and the acetate of 4-tert-butylcyclohexanol [7], on the other.

In changing from bornylcyclohexanone to its homologs, a similar change in smell is observed as in the case of the corresponding alcohols: the character of the smell of bornyl-3-methylcyclohexanone does not change, but becomes weaker, while the smell of bornyl-2-methylcyclohexanone increases sharply and acquires a different, musk-balsam nuance.



EXPERIMENTAL

Preparation of Terpenophenols

Menthylphenol. A mixture of 100 g of menthyl chloride (b.p. 97-100.5° at 12 mm, d_4^{20} 0.9407, n_D^{20} 1.4640) and 600 g of phenol were refluxed for 24 hours, then the greater part of the unreacted phenol was distilled off in steam and the thick, dark brown residue was stirred well with 2 liters of 5% caustic potash solution and extracted with ether. The ether extract was dried with anhydrous sodium sulfate, the ether distilled off and the residue distilled in vacuum. We obtained 112 g (84.2%) of menthylphenol. B.p. 149-154° (2.5 mm), d_4^{40} 0.9874, n_D^{40} 1.5248.

Found %: C 82.48, 82.65; H 10.31, 10.50; OH 7.35, 7.44; $C_{16}H_{24}O$. Calculated %: C 82.68; H 10.41; OH 7.33.

The phenylurethan of menthylphenol (after two recrystallizations from benzine and then from methyl alcohol) formed lustrous plates with m.p. 140° [6, 10].

Bornylphenol. This was prepared similarly to menthylphenol. In the reaction we used 100 g of the mixture of isobornyl and bornyl chlorides and 600 g of phenol. We obtained 88 g (66%) of a product with b.p. 146-157° (0.8 mm) and containing 94.6% of bornylphenol (determined by acetylation with acetic anhydride in the presence of pyridine). For analysis we took a narrower fraction with a 99.6% bornylphenol content. B.p. 154.5-157° (1 mm), d_4^{20} 1.0484, n_D^{20} 1.5505.

Found %: C 83.22, 83.25; H 9.82, 9.64. $C_{16}H_{22}O$. Calculated %: C 83.41; H 9.63.

Bornylphenol 3,5-dinitrobenzoate, m.p. 156.5-157.5° (from a mixture of methyl alcohol and chloroform, 3 : 1 by volume) formed fine, light yellow plates.

Found %: N 6.58, 6.69. $C_{23}H_{24}O_6N_2$. Calculated %: N 6.60.

Bornyl-3-methylphenol. The condensation was carried out as described above. In the reaction we used 100 g of the mixture of isobornyl and bornyl chlorides and 600 g of m-cresol. We obtained 123 g (87.2%) of product with b.p. 175-185° (6 mm) and containing 95.7% of bornyl-3-methylphenol (determined by acetylation).

For analysis we used a narrower fraction with a 99.7% content of bornyl-3-methylphenol. B.p. 163-166° (3.5 mm), d_4^{20} 1.0278, n_D^{20} 1.5470.

Found %: C 83.54, 83.46; H 10.01, 9.99. $C_{17}H_{24}O$. Calculated %: C 83.55; H 9.90.

The 3,5-dinitrobenzoate of bornyl-3-methylphenol, m.p. 154-156° (from a mixture of methyl alcohol and chloroform, 3 : 1 by volume), formed fine, light yellow plates.

Found %: N 6.31, 6.41. $C_{24}H_{26}O_6N_2$. Calculated %: N 6.39.

Bornyl-2-methylphenol. In the reaction we used 132 g of the mixture of chlorides and 680 g of o-cresol. We obtained 127 g of product with b.p. 179-189° (9 mm) and containing ~87% of bornyl-2-methylphenol. For analysis we used a narrower fraction with a 97.5% content of bornyl-2-methylphenol. B.p. 172.5-174° (7 mm), d_4^{20} 1.0261, n_D^{20} 1.5444.

Found %: C 83.72, 83.70; H 10.19, 10.16. $C_{17}H_{24}O$. Calculated %: C 83.55; H 9.90.

The corresponding ether was formed in significantly larger amounts than in all the other cases (see above). On distillation the ether was collected mainly in the head fraction, however a complete separation of it from the terpenophenol resulted in large losses of the latter.

The 3,5-dinitrobenzoate of bornyl-2-methylphenol was a red, viscous oil.

Hydrogenation of Terpenophenols and Acetylation of Terpenocyclohexanols.

Menthylcyclohexanol. 116 g of menthylphenol was hydrogenated under a pressure of 150 atm at 125-165° in the presence of 15 g of Raney nickel and 3 ml of 0.5 N alcoholic potassium hydroxide. After 2 hours, 35 liters of hydrogen (104% of theoretical) had been absorbed. On cooling, the hydrogenation product was dissolved in ether, filtered, dried over anhydrous sodium sulfate, the ether distilled off and the product distilled in vacuum. We obtained 83 g (70%) of product with b.p. 165-168° (4 mm) and containing ~ 98% of menthylcyclohexanol. For analysis we took a fraction:

b.p. 156.5-159.5° (1.5 mm), d_4^{40} 0.9470, n_D^{40} 1.4915, MR_D 72.98; calc. 73.21.

Found %: C 80.78, 80.82; H 12.67, 12.65; OH 7.21. $C_{16}H_{30}O$. Calculated %: C 80.60; H 12.68; OH 7.14.

The phenylurethan of menthylcyclohexanol was prepared by heating 1 g of menthylcyclohexanol and 0.5 g of phenylisocyanate in 5 ml of benzine on a boiling water bath; m.p. 128.5-129° (from benzine), lustrous, plate-like crystals.

Found %: N 3.83, 4.09. $C_{23}H_{35}O_2N$. Calculated %: N 3.92.

Acetylation of menthylcyclohexanol. To a mixture of 15 g of menthylcyclohexanol and 23 g of acetic anhydride was added 5 g of a mixture of acetic anhydride and phosphoric acid, prepared not less than 24 hours earlier from 90 g of acetic anhydride and 10 g of concentrated phosphoric acid. A strong evolution of heat occurred. The next day water was added and after several hours the aqueous layer was separated off and the oil dissolved in ether, washed with 5% soda solution and water and dried over anhydrous sodium sulfate. After distilling off the ether, the residue (17 g) was distilled in vacuum. We obtained 11 g (62.5%) of product with b.p. 157-159° (2.5 mm) and containing 97.6% of ester. For analysis we took a fraction with b.p. 154-155° (1 mm) and containing 99.8% of ester, which crystallized on standing, m.p. 80.2-80.7° (from alcohol).

Found %: C 77.01, 76.82; H 11.61, 11.70. $C_{18}H_{32}O_2$. Calculated %: C 77.09; H 11.50.

Bornylcyclohexanol. 230.5 g of bornylphenol was hydrogenated under a pressure of 170 atm at 125-180° in the presence of 36 g of Raney nickel and 5 ml of 0.5 N alcoholic potassium hydroxide. After 2.5 hours 69.5 liters of hydrogen (103% of theoretical) had been absorbed. We obtained 173 g (73.3%) of bornylcyclohexanol with b.p. 165-175° (3 mm). For analysis we took a narrower fraction.

B.p. 173-174° (3 mm), d_4^{20} 0.9931, n_D^{20} 1.5092, MR_D 71.09; calc. 71.01.
Found %: C 80.96, 81.06; H 12.10, 12.04; OH 7.16, 7.12. $C_{16}H_{28}O$. Calculated %: C 81.29; H 11.94; OH 7.19.

Acetylation of bornylcyclohexanol was carried out as above. From 31 g of bornylcyclohexanol and 46 g of acetic anhydride we obtained 22 g (60.2%) of the acetate of bornylcyclohexanol with b.p. 155-170° (3 mm) and containing 96.6% of ester. For analysis we took a narrower fraction with a 98.7% ester content.

B.p. 155-156° (1.5 mm), d_4^{20} 0.9998, n_D^{20} 1.4913, MR_D 80.70; calc. 80.38.

Found %: C 77.82, 77.29; H 10.83, 10.90. $C_{18}H_{30}O_2$. Calculated %: C 77.65; H 10.86.

Bornyl-3-methylcyclohexanol. 88 g of bornyl-3-methylphenol was hydrogenated under a pressure of 160 atm at 112-157° in the presence of 14 g of Raney nickel. After 1.5 hours, 25.5 liters of hydrogen (105% of theoretical) had been absorbed. We obtained 77 g (85.5%) of bornyl-3-methylcyclohexanol with b.p. 144-148° (4 mm). For analysis we took a narrower fraction.

B.p. 153-154° (5 mm), d_4^{20} 0.9783, n_D^{20} 1.5050, MR_D 75.92; calc. 75.63.

Found %: C 81.23. 81.46; H 12.29, 12.21. $C_{17}H_{30}O$. Calculated %: C 81.53; H 12.08.

Bornyl-2-methylcyclohexanol. 101 g of bornyl-2-methylphenol was hydrogenated under a pressure of 145 atm at 115-142° in the presence of 17 g of Raney nickel. After 1.5 hours 29 liters of hydrogen (104% of theoretical) had been absorbed. We obtained 76 g (73.4%) of bornyl-2-methylcyclohexanol with b.p. 141-151° (3 mm) and containing 95.3% of the alcohol. For analysis we took a narrower fraction.

B.p. 157-158° (5 mm), d_4^{20} 0.9826, n_D^{20} 1.5087, MR_D 76.05; calc. 75.63.

Found %: C 81.81, 81.55; H 11.91, 12.16; OH 6.66. $C_{17}H_{30}O$. Calculated %: C 81.53; H 12.08; OH 6.78.

Oxidation of Terpenocyclohexanols.

Menthylcyclohexanone. A solution of 73 g of $Na_2Cr_2O_7 \cdot 2H_2O$ in 168 g of 50% sulfuric acid was added over 1.5 hours with stirring to 138 g of menthylcyclohexanol in 280 ml of glacial acetic acid and 50 ml of water, while the reaction was cooled as required so that the temperature did not rise above 40°. Then the contents of the flask were stirred for 1 hour at 18° and 1 hour on a water bath at 70-80°, diluted with water and stood until the layers completely separated: the oily layer was separated and the aqueous extracted with ether; the ether extracts were combined with the oily layer, washed with water, soda solution and again with water and dried over anhydrous sodium sulfate. After distilling off the ether, the residue (~ 132 g) was distilled in vacuum; from this we collected fractions: 1st b.p. 129-135° (2.5 mm), 13.5 g – a liquid (containing 70% ketone); 2nd b.p. 135-138° (2.5 mm) (containing 90% ketone), partially crystallized; 3rd b.p. 138-140° (2.5 mm), 55.0 g (containing 95% ketone) completely crystallized.

From the 2nd and 3rd fractions we obtained 58 g of colorless crystals of menthylcyclohexanone; on redistilling the liquid filtrate, we obtained a further 12.5 g of crystalline product. In all we obtained 70.5 g (51.5%) of crystalline menthylcyclohexanone with m.p. 82.5-83° (from alcohol), containing 100.4% ketone (determined by oximation), as lustrous prisms.

Found %: C 81.40, 81.18; H 12.19, 11.96. $C_{16}H_{28}O$. Calculated %: C 81.29; H 11.94.

The oxime of menthylcyclohexanone, m.p. 137.5-138° (from methanol) formed lustrous, square plates.

Found %: N 5.74, 5.75. $C_{16}H_{29}ON$. Calculated %: N 5.57.

The semicarbazone of menthylcyclohexanone crystallized together with solvent (ethyl alcohol), which was only completely removed after drying in a drying cupboard at 105-110°; m.p. 155.5-156.5°, a colorless powder.

Found %: N 14.49, 14.41. $C_{17}H_{31}ON_3$. Calculated %: N 14.32.

The 2,4-dinitrophenylhydrazone of menthylcyclohexanone, m.p. 156.5 -157° (from a mixture of ethyl alcohol and ethyl acetate), formed lustrous, orange rods.

Found %: 13.54, 13.65. $C_{22}H_{32}O_4N_4$. Calculated %: N 13.45.

The liquid fraction (49 g) was, apparently, a mixture of crystalline menthylcyclohexanone and some substances which did not contain a carbonyl group. A 2,4-dinitrophenylhydrazone, prepared from this fraction, melted at 156.5-157°; a mixed melting point with the 2,4-dinitrophenylhydrazone prepared from the crystalline ketone, was not depressed.

Bornylcyclohexanone. From a similar oxidation of 20 g of bornylcyclohexanol we obtained 16 g of product containing 90% of ketone; b.p. 126-135° (0.5 mm). For analysis we took a narrower fraction containing 98% of ketone.

B.p. 133-136° (0.5 mm), d_4^{20} 0.9901, n_D^{20} 1.4998, MR_D 69.60; calc. 69.50.

Found %: C 81.99, 82.15; H 11.41, 11.33. $C_{16}H_{26}O$. Calculated %: C 81. 99; H 11.18.

The semicarbazone of bornylcyclohexanone, m.p. 211-212° (from a mixture of methyl alcohol and chloroform, 3 : 1 by volume), formed fine, lustrous plates.

Found % N: 14.29, 14.43. $C_{17}H_{29}ON_3$. Calculated %: N 14.42.

Bornyl-3-methylcyclohexanone. On oxidizing 47 g of bornyl-3-methylcyclohexanol, we obtained 36.5 g of product with a 92% ketone content and b.p. 150-157° (10 mm). For analysis we took a narrower fraction, containing 97.3% ketone.

B.p. 137-138° (3.5 mm), d_4^{20} 0.9767, n_D^{20} 1.4955, MR_D 74.23; calc. 74.12.

Found %: C 82.00, 82.34; H 11.50, 11.33. $C_{17}H_{28}O$. Calculated %: C 82.20; H 11.36.

The semicarbazone of bornyl-3-methylcyclohexanone, m.p. 201-202.5° (from a mixture of methyl alcohol and chloroform, 3 : 1 by volume), formed fine, lustrous plates.

Found %: N 13.58, 13.77. $C_{18}H_{31}ON_3$. Calculated %: N 13.76.

Bornyl-2-methylcyclohexanone. From 44.5 g of bornyl-2-methylcyclohexanol we obtained 31.5 g of product with a 90% ketone content and b.p. 156-170° (7 mm). For analysis we took a narrower fraction with a 98.5% ketone content:

B.p. 138-140° (4 mm), d_4^{20} 0.9722, n_D^{20} 1.4930, MR_D 74.25; calc. 74.12.

Found %: C 82.22, 82.35; H 11.27, 11.19. $C_{17}H_{28}O$. Calculated %: C 82.20; H 11.36.

The semicarbazone of bornyl-2-methylcyclohexanone, m.p. 203.5-204° (from a mixture of methyl alcohol and chloroform, 3 : 1 by volume), formed fine, snow-white plates.

Found %: N 13.80, 14.04. $C_{18}H_{31}ON_3$. Calculated %: N 13.76.

SUMMARY

1. A series of terpenophenols were synthesized; their conversion into the corresponding terpenocyclohexanols and terpenocyclohexanones resulted in the formation of substances with a very stable and pleasant smell with a cedarlike, sandalwood or musk-balsam nuance.

2. Terpenophenols, containing a bornyl and not a menthyl radical, have greater possibilities in the preparation of aromatic principles.

3. Acetylation of the terpenocyclohexanols resulted in the weakening or total loss of their original smell.

4. In changing from bornylcyclohexanone to bornyl-3-methylcyclohexanone the character of the smell did not change, but due to the heavier molecules, became weaker, while in changing to bornyl-2-methylcyclohexanone it increased sharply, which was due, apparently, to the presence of a tertiary carbon atom, bonded to methyl, next to the ketone group.

Analogous rules have also been established for the corresponding alcohols.

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PHENYLXANTHONES

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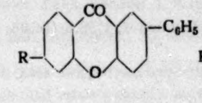
Xanthone is an insecticide [1] and shows toxicity to mites [2], aphids [3], cabbage moths, mosquito larvae, apple leaf-roller larvae, cutworms and termites [4]. The toxicity of xanthone is of a selective nature, since it is not toxic, for example, to honey bees [5]. Until the present time a comparatively small number of substituted xanthone derivatives have been known; many theoretically possible derivatives still remain uninvestigated. In particular, the phenyl-substituted xanthones containing the phenyl group in the 2 and 4 positions of the benzene rings were not known. Introduction of the phenyl radical may affect both the chemical and physiological properties of xanthone.

Proceeding from the information mentioned above, we undertook the synthesis of 2- (I) and 4-phenylxanthone (II). The synthesis of phenylxanthones of such structure can be accomplished by the use of o-hydroxybiphenyl and p-hydroxybiphenyl, which are by-products of the manufacture of phenol [6].



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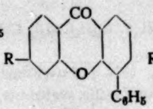

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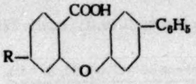

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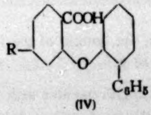

(IV)

R = H or Cl

o-(2-Biphenylyl)oxybenzoic acid (IV) was obtained by the condensation of o-bromobenzoic acid with o-hydroxybiphenyl in the presence of alkali and copper powder. Condensation under the same conditions of o-bromobenzoic acid with p-hydroxybiphenyl gave o-(4-biphenylyl)oxybenzoic acid (III).

Condensation of 2,4-dichlorobenzoic acid with p-hydroxybiphenyl gave 2-(p-biphenylyl)oxy-5-chlorobenzoic acid (III; R = Cl). Cyclization of the biphenylyloxybenzoic acids mentioned with the aid of phosphorus pentoxide in benzene solution gave quantitative yields of the corresponding phenylxanthones.

The same phenylxanthones were obtained in considerably lower yields by heating the biphenylyloxybenzoic acids with concentrated sulfuric acid. Cyclization also took place when the biphenylyloxybenzoic acids were treated with phosphorus pentachloride or thionyl chloride and the acid chlorides formed were subsequently distilled in vacuo.

All of the phenylxanthones obtained showed an intense yellow coloration upon solution in concentrated sulfuric acid, which disappeared when the solution was diluted with water; the phenylxanthones were separated out unchanged by this treatment.

EXPERIMENTAL

Preparation of o-(4-biphenylyl)oxybenzoic acid (III; R = H). 4.5 g of o-bromobenzoic acid was added to a solution of 1 g of sodium in 20 ml of alcohol, and to the mixture were added 17 g of p-hydroxybiphenyl and 0.1 g of copper powder. The alcohol was distilled off and the mixture was heated in an oil bath at 210-230° for 4 hours. The reaction mixture was ground to a powder and treated with a solution of sodium carbonate. The emulsion that formed was extracted with ether. The aqueous layer was acidified with hydrochloric acid. The oil that separated out immediately solidified to a crystalline mass. The product was dissolved in ether and the ethereal solution was extracted with a saturated solution of sodium bicarbonate. Upon acidification with hydrochloric acid, a crystalline, slightly yellow product separated out from the water layer. After crystallization from a mixture of benzene and petroleum ether (1 : 1), o-(4-biphenylyl)oxybenzoic acid was obtained as fine, needle-shaped crystals with m.p. 148-150°.

Found %: C 78.29, 78.37; H 4.77, 4.80. Equiv. 295.0. $C_{19}H_{14}O_3$. Calculated %: C 78.52; H 4.86. Equiv. 290.3.

Preparation of o-(2-biphenylyl)oxybenzoic acid (IV; R = H). 8.2 g of o-(2-biphenylyl)oxybenzoic acid was obtained from 4.5 g of o-bromobenzoic acid and 17.0 g of o-hydroxybiphenyl under the conditions described for the preparation of o-(4-biphenylyl)oxybenzoic acid.

After crystallization from benzene, the product formed fine, colorless needles with m.p. 156-157°.

Found %: C 78.49; H 4.78. Equiv. 292.4. $C_{19}H_{14}O_3$. Calculated %: C 78.52; H 4.86. Equiv. 290.3.

Preparation of o-(4-biphenylyl) oxy-5-chlorobenzoic acid (III; R = Cl). 8.5 g of 2,4-dichlorobenzoic acid was added to a solution of 2.3 g of sodium in 50 ml of methanol, and to the mixture was added 20.0 g of p-hydroxybiphenyl. The methanol was distilled off, 0.1 g of copper powder was added, after which the mixture was heated on an oil bath for 4 hours at 200-230°. The reaction mass was then treated as in the preceding case.

After 3 crystallizations from glacial acetic acid, a product with m.p. 222-224° appeared in the form of colorless, needle-shaped crystals.

Found %: C 70.11; H 4.0; Cl 10.21. Equiv. 326.1. $C_{19}H_{13}O_3Cl$. Calculated %: C 70.5; H 4.04; Cl 10.93. Equiv. 324.76.

Preparation of 4-phenylxanthone (II; R = H). 0.14 g of o-(2-biphenylyl)oxybenzoic acid, 5 ml of benzene and 0.5 g of phosphorus pentoxide were heated with a reflux condenser on a boiling water bath for 2 hours. While cooling, 30 ml of water was added to the reaction mass, the benzene layer was separated and dried with anhydrous sodium sulfate.

After the benzene was distilled off, there remained on the bottom of the flask a yellow oil, which solidified upon standing. The weight of the dried product was 0.13 g.

Recrystallized from methanol, the product formed yellowish needles with m.p. 131-132°. The material was not soluble in alkali, but dissolved in concentrated sulfuric acid with an intense yellow coloration. After dilution of the sulfuric acid solution with water, the color disappeared and the material precipitated as a light yellow, amorphous mass.

Found %: C 83.5; H 4.65. $C_{19}H_{12}O_2$. Calculated %: C 83.84; H 4.41.

Preparation of 2-phenylxanthone (I; R = H). 1.5 g of o-(4-biphenylyl)oxybenzoic acid, 30 ml of benzene and 5.0 g of phosphorus pentoxide were heated with a reflux condenser on a boiling water bath for 2 hours. To the cooled reaction mixture was added 20 ml of water, the benzene layer was separated and dried over sodium sulfate. After the benzene was distilled off, a yellow-colored, brittle mass remained. The dry weight of the product was 1.34 g. After crystallization from acetic acid, 2-phenylxanthone was obtained as slightly yellow-colored, needle-shaped crystals with m.p. 143-145°. The material was insoluble in alkali, and dissolved in concentrated sulfuric acid with an intense yellow coloration.

Found %: C 83.61; H 4.54. $C_{19}H_{12}O_2$. Calculated %: C 83.84; H 4.41.

Preparation of 2-phenyl-6-chloroxanthone (I; R = Cl). 1.5 g of product was obtained from 1.6 g of 2-(p-biphenylyl)oxy-5-chlorobenzoic acid, 5.0 g of phosphorus pentoxide and 30 ml of benzene under the conditions described for the preceding compounds. After crystallization from benzene, the 2-phenyl-6-chloroxanthone formed slightly yellow-colored needles with m.p. 231-232°. The material was insoluble in alkali, and with concentrated sulfuric acid it gave an intense yellow coloration.

Cyclization with the aid of other dehydrating agents. In experiments on the cyclization of o-(2-biphenylyl)oxybenzoic acid by heating with concentrated sulfuric acid, 4-phenylxanthone was obtained in less than half the yield obtained when phosphorus pentoxide was used.

Cyclization of o-(4-biphenylyl)oxybenzoic acid with the aid of phosphorus pentachloride. 1.45 g of o-(4-biphenylyl)oxybenzoic acid was ground with 1.1 g of phosphorus pentachloride in a mortar. The mixture was transferred to a distilling flask and subjected to distillation under the vacuum from a water-jet pump. After the phosphorus oxychloride was distilled off, the distillation was continued at 2 mm; at 240-260° a yellowish oil fraction distilled which solidified in the neck of the flask and the exhaust tube in a crystalline mass. Yield about 1 g. M. p. after crystallization from acetic acid was 143-145°. An experiment using thionyl chloride for the cyclization proceeded in an analogous manner. The yield was also low.

Thus the most favorable method of cyclizing the biphenylyloxybenzoic acids is by heating them with phosphorus pentoxide.

SUMMARY

1. The previously unknown compounds o-(2-biphenylyl)oxybenzoic acid, o-(4-biphenylyl)oxybenzoic acid, and 2-(p-biphenylyl)oxy-5-chlorobenzoic acid have been prepared.

2. It has been shown that the cyclization of the biphenylyloxybenzoic acids listed goes smoothly with the formation of the previously unknown 2-phenylxanthone, 4-phenylxanthone and 2-phenyl-6-chloroxanthone.

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NITRATION OF 2-METHYL-5-AMINOPYRIDINO-(2,3-d)-THIAZOLE

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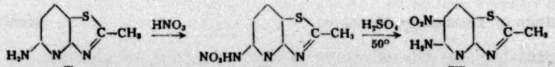
The behavior of pyridinothiazoles and their derivatives toward different reagents has received almost no study. It is known that when pyridinothiazoles are heated with alkali, cleavage of the thiazole ring occurs with the formation of the corresponding o-aminomercaptopyridines [1]. 2-Alkylpyridinothiazoles upon reaction with permanganate form the corresponding pyridinothiazolcarboxylic acid [2]. By treatment with alkylating agents, mono- and diquaternary salts are obtained [3]. The behavior of the pyridinothiazoles and their substitution products with nitric and sulfuric acids, halogens, and other reagents has not been studied.

Our objective in the present work was to ascertain the action of concentrated nitric acid on the pyridinothiazoles. Because of the comparatively greater ease of obtaining only one mononitro derivative, we chose for investigation 2-methyl-5-aminopyridino-(2,3-d)-thiazole (I), the acetyl derivative of which has been described in the literature [4].

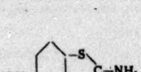
Experiments on the nitration of 2-methyl-5-aminopyridino-(2,3-d)-thiazole showed that it behaves in a manner similar to 2-aminopyridine with nitric acid. Thus, a nitro compound is not produced by the action of concentrated nitric acid on 2-methyl-5-acetamidopyridino-(2,3-d)-thiazole. 2-Acetamidopyridine behaves similarly [5].

2-Methyl-5-aminopyridino-(2,3-d)-thiazole (I), like 2-aminopyridine [6], forms 2-methyl-5-nitraminopyridinothiazole (II); the latter rearranges to 2-methyl-5-amino-6-nitropyridino-(2,3-d)-thiazole (III) at 50° in concentrated sulfuric acid.

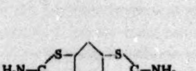


(I) (II) (III)

To obtain the starting material, 2-methyl-5-aminopyridino-(2,3-d)-thiazole (I), we used 2,6-diaminopyridine, which we converted through the thiocyanate to 2,5-diaminopyridino-(2,3-d)-thiazole (IV); the latter, by cleavage with alkali and subsequent condensation with acetic anhydride, was converted to 2-methyl-5-acetamido-(2,3-d)-thiazole. By saponification of the acetyl derivative with dilute hydrochloric acid, compound (I) was obtained.



(IV)



(V)

2,5-Diaminopyridino-(2,3-d)-thiazole (IV) was first prepared by Bernstein and co-workers [7] in 24% yield with m.p. 138-139°; Jamamoto and Takahashi [8] showed a yield of 19% and m.p. 137°. Usually products are obtained in good yields from thiocyanation; for this reason it was of some interest to ascertain the cause for the small yield of compound (IV).

When we carried out the thiocyanation of 2,6-diaminopyridine under the conditions described in the literature [7] for the preparation of 2,5-diaminopyridinothiazole (using 1 mole of bromine to 1 mole of 2,6-diaminopyridine), we discovered that two products were formed as a result of this reaction – the expected 2,5-diaminopyridino-(2,3-d)-thiazole (I) with m.p. 138-139°, easily soluble in hot water, and a material that was insoluble in water. The reaction product which was insoluble in water dissolved in dilute hydrochloric acid and was precipitated from the acid solution by an aqueous solution of ammonia. After crystallizing it from ethylene glycol, we obtained light yellow needles that did not melt upon heating to 300°. This product appeared to be identical with diaminodithiazolylpyridine (V), obtained by Bernstein et al. [7] by the action of 2 moles of bromine on 2,6-diaminopyridine in the presence of an excess of potassium thiocyanate. Therefore, by the thiocyanation of 2,6-diaminopyridine using 1 mole of bromine, compound (V) was produced in 43% yield, as well as 2,5-diaminopyridinothiazole (IV).

It was also ascertained that 2,5-diaminopyridinothiazole (IV) was very easily split not only by heating in sodium hydroxide solution, but also by brief boiling with an aqueous solution of sodium carbonate. If the precipitate of crude compound (IV) obtained by neutralization of the reaction mixture, after thiocyanation, with solid sodium carbonate was carefully washed free of excess of the latter, then the yield of pure 2,5-diaminopyridino-(2,3-d)-thiazole could be increased from 24 to 42-45%.

EXPERIMENTAL

2-Methyl-5-acetamidopyridino-(2,3-d)-thiazole was prepared by Takahashi and Ueda [4] in the amount of 0.47 g. Since we needed a larger amount of this pyridinothiazole derivative, we changed the method of preparation a little. 20 g of 2,5-diaminopyridino-(2,3-d)-thiazole in 150 ml of 10% aqueous sodium hydroxide solution was boiled for 3 hours until the evolution of ammonia ceased, the solution was cooled and neutralized with acetic acid. To the neutral mixture was added 30 ml of acetic anhydride, and it was then boiled for 1 hour. The acyl derivative of 2,6-diamino-3-mercaptopyridine that formed was not separated, but the solution was evaporated to dryness under the vacuum of a water pump, then another 30 ml of acetic anhydride was added to the dry, solid residue and the mixture was heated to boiling for 2 hours. The excess of acetic anhydride was removed in vacuo on a water bath, the residue was made alkaline with ammonia, and the 2-methyl-5-acetamidopyridino-(2,3-d)-thiazole was repeatedly extracted with chloroform. After distilling off the chloroform, the preparation was purified by recrystallization from methyl alcohol (with carbon). Yield 10.5 g (42%), m.p. 247°, which agrees with the data in the literature [4].

2-Methyl-5-aminopyridino-(2,3-d)-thiazole (IV) was obtained by heating 12.5 g of 2-methyl-5-acetamidopyridino-(2,3-d)-thiazole with 30 ml of concentrated hydrochloric acid on a boiling water bath for 1 hour. After distilling off the acid under the vacuum from a water pump, the solid residue was made alkaline with a 40% solution of sodium hydroxide and extracted several times with chloroform. The chloroform solution was concentrated to a volume of 25-30 ml and passed through a column of alumina 15 cm in height and 2 cm in diameter. The column was eluted with chloroform. After removal of the solvent, there remained 8.7 g of snow-white crystals of 2-methyl-5-aminopyridino-(2,3-d)-thiazole with m.p. 170°. Treatment of these crystals with an ether solution of hydrogen chloride produced the hydrochloride, which was recrystallized from methyl alcohol. Colorless needles were obtained with m.p. 247°, agreeing with the data in the literature [4].

Nitration of 2-methyl-5-acetamidopyridino-(2,3-d)-thiazole. a) Nitration at 0°. 1.5 ml of nitric acid (d 1.5) was added dropwise to a solution of 3 g of 2-methyl-5-acetamidopyridino-(2,3-d)-thiazole in 20 ml of concentrated sulfuric acid at 0° while slowly stirring. After standing for an hour in the cooling mixture, the solution was poured onto ice and neutralized with an aqueous ammonia solution. The precipitate was filtered off, washed with water, and dried. The weight was 2.9 g. Recrystallized from methyl alcohol it melted at 247° and gave no depression in mixed melting point with the starting material, 2-methyl-5-acetamidopyridino-(2,3-d)-thiazole.

b) Nitration at room temperature. 1.5 ml of nitric acid (d 1.5) was added dropwise to a solution of 3 g of 2-methyl-5-acetamidopyridino-(2,3-d)-thiazole in 20 ml of concentrated sulfuric acid at room temperature while slowly stirring. The temperature of the reaction mixture during nitration rose to 25-28°. After standing for an hour, the solution was poured onto ice. The precipitate that separated was filtered off and dried. The weight of the precipitate was 1.6 g. Only a small part of the precipitate dissolved in alcohol; the insoluble portion was recrystallized from acetic acid. Colorless needles were obtained that did not melt up to 270°. The analysis of this material corresponded with the nitrate of 2-methyl-5-acetamidopyridino-(2,3-d)-thiazole.

Found %: N 20.71, 20.47. $C_{10}H_{10}O_4N_4S$. Calculated %: N 20.74.

The crystals that had separated from the alcohol solution appeared non-homogeneous. It was possible to separate them by fractional crystallization from methyl alcohol. Substances with m.p. 216° and m.p. 186° (decomp.) were obtained. The first of these substances did not dissolve in alkali but the second one dissolved very readily even in sodium carbonate solution.

It was established by further experiments that the crystals with m.p. 216° were 2-methyl-5-amino-6-nitropyridino-(2,3-d)-thiazole and the crystals with m.p. 186° (decomp.) were 2-methyl-5-nitraminopyridino-(2,3-d)-thiazole.

On the basis of the data presented, it was concluded that 2-methyl-5-acetamidopyridino-(2,3-d)-thiazole, like 2-acetamidopyridine, does not form a nitro product when treated with nitric acid. However, at room temperature (25-28°) in sulfuric acid solution hydrolysis of the acetamido group occurs and the 2-methyl-5-aminopyridinothiazole that has been formed is nitrated like 2-aminopyridine. First the nitramine is formed, which then rearranges to the nitraminopyridinothiazole. Experiments on the nitration of 2-methyl-5-aminopyridino-(2,3-d)-thiazole fully confirmed this conclusion.

Nitration of 2-methyl-5-aminopyridino-(2,3-d)-thiazole. 5.5 g of 2-methyl-5-aminopyridino-(2,3-d)-thiazole was added in small portions, with energetic stirring, to 50 ml of concentrated sulfuric acid. Stirring was continued until the material completely dissolved. Then 7.5 ml of nitric acid (d 1.5) was added drop by drop. The temperature of the reaction mixture at the same time rose to 26-29°. On completion of the addition of the nitric acid, the mixture was allowed to stand for an hour and then was poured onto ice, neutralized with 40% sodium hydroxide solution to pH 5, and the precipitate that separated was filtered off, washed with water and dried. The weight of the precipitate was 5.9 g. After recrystallization from alcohol, small yellow needles precipitated which decomposed at 186° with a flash. Analysis for nitrogen indicated a low nitrogen content, which is characteristic of nitramines and nitraminothiazoles [9].

Found %: N 25.90, 25.61. $C_7H_6O_2N_4S$. Calculated %: N 26.66.

The crystals that decomposed at 186°, corresponding to 2-methyl-5-nitraminopyridinothiazole (II), were soluble in alkali and could be recrystallized from hot water. The same properties are characteristic of 2-nitraminopyridine. Rearrangement of 2-methyl-5-nitraminopyridino-(2,3-d)-thiazole to 2-methyl-5-amino-6-nitropyridinothiazole was carried out under the conditions used for the isomerization of 2-nitraminopyridine. 3 g of 2-methyl-5-nitraminopyridinothiazole (decomp. 186°) was added in small portions, with stirring, to 25 ml of concentrated sulfuric acid, the mixture was heated on a water bath at 50° for 1 hour, then allowed to stand at room temperature for 3 hours, poured over ice, and neutralized with 40% sodium hydroxide solution. The precipitate that separated was filtered off, washed with water, and dried. The weight of the precipitate was 2.7 g; after recrystallization from alcohol, 2-methyl-5-amino-6-nitropyridinothiazole (III) was obtained in the form of orange needles with m.p. 216°. Analysis for nitrogen gave a low content; the sulfur content corresponded to the calculated amount.

Found %: N 25.77, 25.87; S 15.47, 15.37, $C_7H_6O_2N_4S$. Calculated %: N 26.66; S 15.23.

SUMMARY

It has been shown that nitration of 2-methyl-5-aminopyridino-(2,3-d)-thiazole leads to the formation of 2-methyl-5-nitraminopyridino-(2,3-d)-thiazole, which upon heating in sulfuric acid rearranges to 2-methyl-5-amino-6-nitropyridino-(2,3-d)-thiazole.

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DERIVATIVES OF PYRIDINO-(2,3-d)-THIAZOLE

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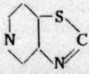
In previous papers we have described the synthesis of pyridino-(4,3-d)-thiazole-2-carboxylic acid (I) [1], its ester, amide, and hydrazide, and also derivatives of pyridino-(3,2-d)-thiazole-2-carboxylic acid (II) [2], for the purpose of ascertaining the effect of these compounds on the tuberculosis bacillus.

In the present work we had in view the preparation of analogous derivatives of the isomeric pyridino-(2,3-d)-thiazole-2-carboxylic acid (III) for the same purpose.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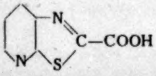
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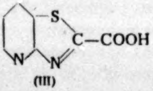
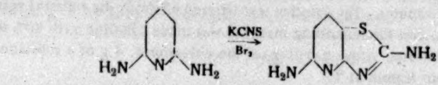

(III)

The starting material, 2-methylpyridino-(2,3-d)-thiazole, has been described. It was obtained by Takahashi et al. [3] by the oxidation of 2-thioacetamidopyridine with potassium ferricyanide in alkaline medium. Derivatives of 2-methylpyridino-(2,3-d)-thiazole substituted in the 6 position were obtained, according to the data of Takahashi et al. [4], by the oxidation of the corresponding 5-substituted thioacetamidopyridine under analogous conditions. The work of Takahashi and his coworkers was published in a journal that was not accessible to us and we were able to use only the data given in the abstract [3].

Our repeated attempts to prepare 2-methylpyridino-(2,3-d)-thiazole by the method indicated by Takahashi, the oxidation of 2-thioacetamidopyridine with potassium ferricyanide in alkaline medium, unfortunately proved to be unsuccessful. The unchanged starting material, 2-thioacetamidopyridine, and its saponification product, 2-acetamidopyridine, were recovered from the reaction. This unsuccessful attempt to prepare 2-methylpyridino-(2,3-d)-thiazole by the cyclization of 2-thioacetamidopyridine was not unexpected. It was well known that all attempts to prepare 1,8-naphthyridine from 2-aminopyridine by cyclization by the method of Skraup or by other methods had proved unsuccessful.

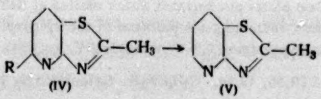
It was conclusively shown by the work of Chichibabin and Seide [5] in 1924-1928 that ring closure in 2-acylamido derivatives of pyridine takes place at the nitrogen atoms of the nucleus with the formation of pyrimidine derivatives, and not in the β-position with the formation of 1,8-naphthyridine. In connection with investigations on the cyclization of 2-aminopyridine I. L. Knunyants and D. A. Katrenko [6] had already published in 1940 work in which they studied the possibility of the cyclization of 2-thioacetamidopyridine by oxidation with potassium ferricyanide in alkaline medium and also with other oxidizing agents. As a result of their experiments, the authors came to the conclusion that in this case ring closure does not take place in the 3 position of the pyridine nucleus, and the expected pyridinothiazole is not formed. These facts are explained by the properties of the pyridine ring; in the pyridine molecule the electrons are drawn from the 2- and 4-carbon atoms to the nitrogen atom, and in less degree from the 3-atom; the electron density near the carbon atom in position 3 is greater than near the carbon atoms in positions 2 or 4, but it is insufficient for closure to take place on the 3-carbon; as a result of this, ring closure takes place at the nitrogen atom of the nucleus with the formation of pyrimidine derivatives, or it does not take place at all, as in the case of the oxidation of 2-thioacetamidopyridine. It is another matter if there is an electron donor group, for example the amino group, in the 6 position of the pyridine. The electron density near the carbon in the 3 position becomes sufficient for ring closure in this place [7]. Consequently, cyclization of 2,6-diaminopyridine by the method of Skraup produces derivatives of 1,8-naphthyridine in good yield.

These considerations make it understandable why thiocyanation of 2,6-diaminopyridine leads to the formation of 2,5-diaminopyridino-(2,3-d)-thiazole,



but 2-amino-5-substituted pyridines do not undergo thiocyanation [8]. The indication by Takahashi et al. [9] that 2-amino-6-nitropyridino-(2,3-d)-thiazole is formed by the thiocyanation of 2-amino-5-nitropyridine apparently is in error. Subsequently the authors themselves refuted the possibility of the conversion of 2-amino-5-bromo(or 5-iodo)-pyridine by thiocyanation into 2-amino-6-bromo(or 6-iodo)-pyridino-(2,3-d)-thiazole [8] described by them earlier [9].

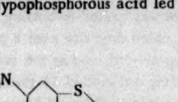
Thus, to obtain the 2-methylpyridino-(2,3-d)-thiazole (V) in which we were interested, it was necessary to choose another method. We decided to prepare this pyridinothiazole by means of the deamination of 2-methyl-5-aminopyridino-(2,3-d)-thiazole (IV, R = NH$_2$).



(IV) (V)

The series of experiments set up showed that 2-methyl-5-aminopyridino-(2,3-d)-thiazole and 2-aminopyridine have analogous properties with respect to their behavior not only with nitric acid, as we had shown previously [10], but also with nitrous acid. It was known that attempts to prepare azo dyes from 2-aminopyridine by the use of nitrous acid under the usual conditions were not successful; diazotization of 2-aminopyridine led to the formation of 2-hydroxypyridine [11]. Diazotization of 2-methyl-5-aminopyridino-(2,3-d)-thiazole (IV, R = NH$_2$) with sodium nitrite in alcohol in the presence of concentrated sulfuric acid led to the formation of 2-methyl-5-ethoxypyridino-(2,3-d)-thiazole (IV, R = OC$_2$H$_5$) instead of the expected 2-methylpyridino-(2,3-d)-thiazole (V). Diazotization of 2-methyl-5-aminopyridino-(2,3-d)-thiazole in concentrated sulfuric acid with subsequent reduction by hypophosphorous acid led to the formation of the 5-hydroxy derivative (IV, R = OH). 2-Methyl-5-chloropyridino-(2,3-d)-thiazole (IV, R = Cl) was obtained by diazotization in hydrochloric acid in the presence of hypophosphorous acid.

Analogously, the diazotization of 2-methyl-5-amino-6-nitropyridino-(2,3-d)-thiazole in dilute hydrochoric acid at −10° with subsequent treatment with hypophosphorous acid led to the formation of 2-methyl-5-hydroxy-6-nitropyridino-(2,3-d)-thiazole (VI).



(VI)

The indicated properties of 2-methyl-5-aminopyridino-(2,3-d)-thiazole were the reason for our lack of success in preparing 2-methylpyridino-(2,3-d)-thiazole (V) by the projected method.

EXPERIMENTAL

Action of nitrous acid on 2-methyl-5-aminopyridino-(2,3-d)-thiazole (IV, R = NH_2) in alcohol. 10 ml of concentrated sulfuric acid was introduced, drop by drop, into a solution of 6.4 g of 2-methyl-5-aminopyridino-(2,3-d)-thiazole [10] in 75 ml of alcohol while cooling and stirring. To the white precipitate that formed was added slowly, at 10°, a solution of 4.1 g of sodium nitrite in 7.5 ml of water. Stirring was continued for 1 hour after the addition of the sodium nitrite, then the mixture was gradually heated to boiling on a water bath and the boiling was continued for 15 minutes. The solution was filtered off from the mineral residue, the alcohol was distilled off from the filtrate, and the remaining material was made alkaline with 40% sodium hydroxide solution and extracted with chloroform. After distilling off the chloroform, 4 g of a substance remained that melted after recrystallization from ligroin at 71°.

Analysis for nitrogen confirmed the formation of 2-methyl-5-ethoxypyridino-(2,3-d)-thiazole (IV, R = OC_2H_5) instead of the expected 2-methylpyridino-(2,3-d)-thiazole.

Found %: N 14.50, 14.32. $C_9H_{10}ON_2S$. Calculated %: N 14.43.

Action of nitrous acid on 2-methyl-5-aminopyridino-(2,3-d)-thiazole in concentrated sulfuric acid. 2 g of sodium nitrite was added in small portions, while stirring, to 30 ml of concentrated sulfuric acid. The solution was cooled to −10° and at this temperature there was slowly added, dropwise, over a period of 45 minutes 1.65 g of 2-methyl-5-aminopyridino-(2,3-d)-thiazole in 10 ml of concentrated sulfuric acid, then 5.3 g of sodium hypophosphite in 25 ml of concentrated sulfuric acid was added with vigorous stirring. The mixture was kept at 0° for 20 hours, then poured over ice (300 g), and from the solution thus obtained a substance was extracted with chloroform. After distilling off the chloroform, 1.2 g of a solid remained which was recrystallized from alcohol with carbon. Colorless plates precipitated which melted at 243°. They were poorly soluble in water, but readily soluble in dilute alkalies, indicating the presence of the hydroxyl group. Analytical data confirmed the formation of 2-methyl-5-hydroxypyridino-(2,3-d)-thiazole (IV, R = OH).

Found %: N 16.30, 16.39; S 19.55, 19.64. $C_7H_6ON_2S$. Calculated %: N 16.86; S 19.25.

Action of nitrous acid on 2-methyl-5-aminopyridino-(2,3-d)-thiazole in hydrochloric acid. 1.3 g of sodium nitrite in 4 ml of water was slowly added dropwise, while stirring, at 0° to a solution of 2 g of 2-methyl-5-aminopyridino-(2,3-d)-thiazole in dilute hydrochloric acid (10 ml of concentrated hydrochloric acid and 5 ml of water). Upon completion of the addition, stirring was continued for 30 minutes longer, then the mixture was heated on the water bath to boiling, the solution was cooled and neutralized with sodium carbonate and repeatedly extracted with chloroform. The chloroform was concentrated to a volume of 30-35 ml and passed through a layer of alumina, 12 cm in height and 2 cm in diameter. The material was eluted with chloroform. After the solvent was distilled off, there remained 1.6 g of light yellow crystals with m.p. 169-170°. The compound recrystallized from ligroin contained halogen. Analytical data confirmed the formation of 2-methyl-5-chloropyridino-(2,3-d)-thiazole (IV, R = Cl).

Found %: N 15.31, 15.12; Cl 19.39, 19.48. $C_7H_5N_2SCl$. Calculated %: N 15.16; Cl 19.24.

Action of nitrous acid on 2-methyl-5-amino-6-nitropyridino-(2,3-d)-thiazole. 0.7 g of 2-methyl-5-amino-6-nitropyridinothiazole [10] was added to dilute hydrochloric acid (10 ml of concentrated acid and 20 ml of water), and to obtain solution the mixture was heated to boiling, then 10 ml more of concentrated hydrochloric acid was added. To the clear solution was added dropwise over a period of 20 minutes a solution of 0.25 g of sodium nitrite in 2 ml of water, with stirring at −10°, and at the same temperature a solution of 1.8 g of sodium hypophosphite in 5 ml of water was added over a period of 15 minutes. Stirring at −5 to 0° was continued for an hour more, then the reaction mixture was left at 0° for 20 hours. The yellow precipitate that had separated out was filtered off, washed with water, with dilute alkali solution, with water again, and dried. The weight of the precipitate was 0.56 g. It was difficultly soluble in alcohol, and was recrystallized from acetic acid. The yellow needles melted at 288°. According to the analysis for nitrogen, the substance was 2-methyl-5-hydroxy-6-nitropyridino-(2,3-d)-thiazole (VI).

Found %: N 19.60, 19.68. $C_7H_5O_3N_3S$. Calculated %: N 19.90.

SUMMARY

1. It has been shown that 2-methylpyridino-(2,3-d)-thiazole is not obtainable by deamination of 2-methyl-5-aminopyridino-(2,3-d)-thiazole.

2. By diazotization of 2-methyl-5-aminopyridino-(2,3-d)-thiazole under different conditions, 2-methyl-5-hydroxy-, 2-methyl-5-ethoxy-, and 2-methyl-5-chloropyridino-(2,3-d)-thiazoles were obtained.

3. 2-Methyl-5-amino-6-nitropyridino-(2,3-d)-thiazole was converted by diazotization in hydrochloric acid solution into 2-methyl-5-hydroxy-6-nitropyridino-(2,3-d)-thiazole.

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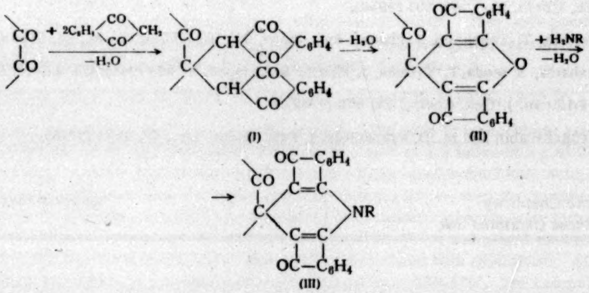
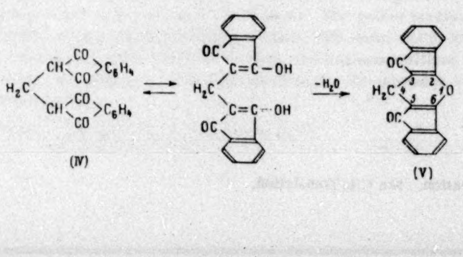
CYCLIZATION OF METHYLENEDI(INDANDIONE)

L. S. Geita and G. Ya. Vanag

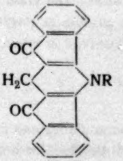
In our previous papers [1-4] it has been shown that phenanthraquinone, acenaphthoquinone, and their nitro derivatives are easily condensed with 1,3-indandione; during this process a molecule of water splits out from one carbonyl group of the quinones mentioned and two molecules of indandione, and the corresponding diindandione derivative (I) is formed. The latter under more severe conditions loses another molecule of water and gives the corresponding spiropyran (II). Its oxygen bridge upon reaction with ammonia or amines is replaced by nitrogen to produce the spirodihydropyridine derivative (III). This whole conversion process is illustrated in the following diagram:



It was desirable to investigate whether the reactions mentioned also take place with the simpler diindandione derivatives. For this purpose we chose methylenedi(indandione) (IV), which had already been prepared by Radulescu and Georgescu [5] by the condensation of indandione with formaldehyde in alkaline medium. Methylenedi(indandione) serves as a prototype of this class of compounds; on its carbon atom that connects the two indandione groups there are two hydrogen atoms. It appears that methylenedi(indandione) also closes the pyran ring very readily in solution in acetic anhydride in the presence of sodium acetate to form 2,3(CO), 6,5(CO)-dibenzoylenepyran (V):



Upon heating with alkali dibenzoylenepyran splits with the formation of salts of methylenedi(indandione). Derivatives of dibenzoylenedihydropyridine (VI) are easily formed by heating with ammonia or aliphatic amines in alcohol solution. This compound is sometimes produced by heating methylenedi(indandione) with ammonia. In the cold the soluble ammonium salt of methylenedi(indandione) is formed, which upon heating the solution is cyclized to the insoluble dibenzoylenedihydropyridine that precipitates from the solution as orange-red crystals.



(VI–X)

(VI) R = H,
(VII) R = NO,
(VIII) R = C_2H_5,
(IX) R = $CH_2CH_2CH_2CH_3$,
(X) R = CH_2CH_2OH.

Dibenzoylenedihydropyridine readily yields a nitroso derivative (VII). The products of reaction of dibenzoylenepyran with ethylamine (VIII), n-butylamine (IX) and monoethanolamine (X) were prepared. As yet it has not been possible to separate the reaction product with aniline. Thus, it is easy to convert the simply prepared diindandione derivatives to complex derivatives of pyran and dihydropyridine.

EXPERIMENTAL

Ammonium salt of methylenedi(indandione). a) Methylenedi(indandione) was ground in a mortar with concentrated ammonia. The material became red. Alcohol was added and the mixture was ground and filtered. Orange plates of the monoammonium salt of methylenedi(indandione) crystallized slowly from the filtrate.

b) To a solution of methylenedi(indandione) in acetone was added a little concentrated ammonia. Pure monoammonium salt of methylenedi(indandione) precipitated. M.p. 144°.

Found %: N 4.46. $C_{19}H_{12}O_4 \cdot NH_3$. Calculated %: N 4.37.

The salt dissolved in cold water with a yellow color; it also was soluble in alcohol and slightly so in acetone. Upon heating with alkali ammonia was evolved. Upon acidification a precipitate of methylenedi(indandione) separated out, m.p. 202-203°. When an aqueous solution of the ammonium salt was heated, diindandionedihydropyridine (VI) precipitated.

2,3(CO), 6,5(CO)-Dibenzoylenepyran. 10 g of methylenedi(indandione), 25 ml of acetic anhydride, and a little sodium acetate were heated to boiling, and then maintained on a water bath for 30 minutes. A finely crystalline precipitate of dibenzoylenepyran (V) formed. It was separated by cooling, and washed with glacial acetic acid and alcohol. Yield 6.7 g (71.2%), m.p. 339°. The compound was only slightly soluble in organic solvents. It dissolved in alkalies upon heating with cleavage of the oxygen bridge; when the solution was cooled, the salt of methylenedi(indandione) precipitated. It dissolved in concentrated sulfuric acid with a red-violet coloration.

Found %: C 79.22; H 3.49. $C_{19}H_{10}O_3$. Calculated %: C 79.71; H 3.49.

2,3(CO),6,5(CO)-dibenzoylene-1,4-dihydropyridine (VI). a) 1.5 g of dibenzoylenepyran, 30 ml of alcohol, and 1 ml of concentrated ammonia were heated on a water bath. The material partially dissolved with a red coloration, and partially was immediately converted into red-orange, needle-shaped crystals. The mixture was heated for 15 minutes and the crystals were separated. The yield of dibenzoylenedihydropyridine (VI) was 0.95 g, m.p. 304-306°. It was insoluble in water, soluble in dioxane, chloroform, and glacial acetic acid, slightly soluble in other solvents, readily in pyridine. It dissolved slightly in concentrated hydrochloric acid with an orange color. Upon heating it dissolved a little in alkali. In alcoholic alkali it dissolved with a red color.

Found %: N 5.27. $C_{19}H_{11}O_2N$. Calculated %: N 4.91.

b) 10 g of methylenedi(indandione), 100 ml of alcohol, and 10 ml of concentrated ammonia were boiled for 30 minutes. At first the orange ammonium salt of methylenedi(indandione) formed, which then was converted to the red dibenzoylenedihydropyridine. Yield 6.1 g. The precipitate was boiled with alcohol to free it from possible contamination with the ammonium salt. The material that remained melted at 304-306°.

Found %: N 4.90. $C_{19}H_{11}O_2N$. Calculated %: N 4.91.

N-Nitrosodibenzoylenedihydropyridine (VII). 100 ml of glacial acetic acid was poured over 3 g of dibenzoyldihydropyridine and sodium nitrite was added in small portions over a period of several hours. The starting material gradually went into solution and the nitroso derivative partially precipitated as orange crystals. The mixture was diluted with water and the precipitate was separated. The yield of N-nitrosodibenzoylenedihydropyridine (VII) was 2.5 g, m.p. 175°. The product was readily soluble in glacial acetic acid, alcohol and acetone. It crystallized from alcohol as fine orange crystals. It also dissolved in ether. It gave a positive Lieberman reaction for the nitroso group.

Found %: N 8.75. $C_{19}H_{10}O_3N_2$. Calculated %: N 8.92.

N-Ethyldibenzoylenedihydropyridine (VIII). 2 g of dibenzoylenepyran and 15 ml of a 10% alcoholic solution of ethylamine were boiled for 30 minutes. The material dissolved with a red color. Upon cooling, red needle-shaped crystals of N-ethyldibenzoylenedihydropyridine (VIII) separated. Yield 1.7 g (78.1%), m.p. 230-232°. The compound was highly soluble in organic solvents. It was insoluble in water. It dissolved in concentrated hydrochloric acid readily with an intense red color. The hydrochloride was isolated as dark red needle-shaped crystals. They decomposed in air with the evolution of hydrogen chloride.

Found %: N 4.40. $C_{21}H_{15}O_2N$. Calculated %: N 4.47.

N-n-Butyldibenzoylenedihydropyridine (IX). 3 g of dibenzoylenepyran and 15 ml of a 10% alcoholic solution of n-butylamine were boiled for 10 minutes. All the material dissolved. Upon cooling, shining red crystals of N-n-butyldibenzoylenedihydropyridine (IX) separated. Yield 2.63 g (73.5%), m.p. 210°. The product was insoluble in water and alkalies, slowly soluble in concentrated hydrochloric acid. Upon heating it was highly soluble in alcohol, acetone, and benzene.

Found %: N 4.09, 3.91. $C_{21}H_{19}O_2N$. Calculated %: N 4.10.

N-Ethyloldibenzoylenedihydropyridine. 5 g of dibenzoylenepyran and 30 ml of a 10% alcoholic solution of monoethanolamine was boiled. All of the material dissolved. From the filtrate there separated red crystals of N-ethyloldibenzoylenedihydropyridine (X). Yield 4.5 g (78.2%), m.p. 240-242°. The compound was insoluble in water and alkalies, soluble in concentrated hydrochloric acid. The hydrochloride was isolated as dark red crystals, which readily decomposed with the evolution of hydrogen chloride. Compound (X) was highly soluble in the usual organic solvents, slightly in carbon tetrachloride.

Found %: N 4.18, 4.37. $C_{21}H_{15}O_3N$. Calculated %: N 4.25.

SUMMARY

Methylenedi(indandione) is easily cyclized to the pyran ring by the action of acetic anhydride and sodium acetate. The dibenzoylenepyran thus obtained is converted by the action of ammonia or primary amines to dibenzoylenedihydropyridine or its N-substituted derivatives. Thus, it is possible to easily convert the readily prepared methyenedi(indandione) to the complex pyran and dihydropyridine derivatives.

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CYCLOHEXANONE COMPOUNDS OF MONOSES AND POLYHYDRIC ALCOHOLS

III. DICYCLOHEXYLIDENE-DULCITOL

V. F. Kazimirova

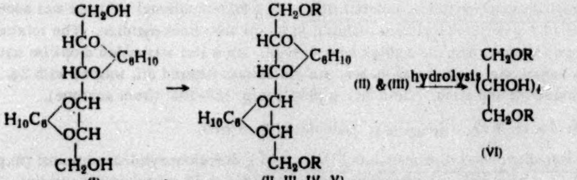
Crystalline dicyclohexylidene-dulcitol has been described earlier [1], but its structure was not proved. The cyclohexanone compounds of glucose [2] and sorbose [3] have structures analogous to the structures of the corresponding acetone compounds.

It was considered of interest to determine the position of the free hydroxyl groups in dicyclohexylidene-dulcitol.

Diacetone-dulcitol, synthesized by Speier [4] and studied by E. Fischer [5], proved to be a mixture of two compounds of identical composition but with different melting points; one of these was named α-diacetone-dulcitol and the other β-diacetone-dulcitol. By using 1.5% hydrochloric acid for the condensation, E. Fischer obtained the α-form and by using 0.5% hydrochloric acid he obtained the β-form. Later R. M. Hann and co-workers [6] showed that the α-form contains free hydroxyl groups on the 1 and 4 carbon atoms, while the β-form contains free hydroxyl groups on the 1 and 6 atoms. Suggested structure for the α-form: 2,3 : 4,6- or 2,5 : 3,6-diacetone-dulcitol; and for the β-form: 2,3 : 4,5- or 2,4 : 3,5- or 2,5 : 3,4-diacetone-dulcitol.

The aim of the present work was to study the structure of dicyclohexylidene-dulcitol (I) and synthesize its derivatives. A description is given of the synthesis of diacetyl-dicyclohexylidene-dulcitol (II), dibenzoyl-dicyclohexylidene-dulcitol (III) and ditosyl-dicyclohexylidene-dulcitol (IV). Dicyclohexylidene-dulcitol is not oxidized by lead tetraacetate in glacial acetic acid solution; the free OH-groups are therefore not adjacent. On the basis of the data obtained it may be concluded that the primary OH-groups are free, since dicyclohexylidene-dulcitol condenses with trityl chloride (triphenylmethyl chloride) with the formation of ditrityl-dicyclohexylidene-dulcitol (V).

The method worked out by S. N. Danilov and I. S. Lishansky [7] for the synthesis of the tosyl ester of α-methylglucose was used for the synthesis of the tosyl ester (IV) and the purification of technical toluenesulfonyl chloride.



(I) (II, III, IV, V) (VI)

(II) $R = COCH_3$; (III) $R = COC_6H_5$; (IV) R = p-Ts; (V) R = Tr; (VI) $R = COCH_3$ or COC_6H_5.

The cyclohexylidene group is more strongly bound to the dulcitol than the isopropylidene group. The hydrolysis of diacetyl-dicyclohexylidene-dulcitol and dibenzoyl-dicyclohexylidene-dulcitol takes place in more severe conditions than the hydrolysis of diacetyl-diacetone-dulcitol and dibenzoyldiacetone-dulcitol [8]. The considerably greater stability of the cyclohexanone compounds, compared with the acetone compounds, was also observed by M. Kh. Gluzman and N. P. Klyushnik [9] for dicyclohexylidene-glucose.

The hydrolysis of diacetyl-dicyclohexylidene-dulcitol (II) and dibenzoyldicyclohexylidene-dulcitol (III) yielded 1,6-diacetyl- and 1,6-dibenzoyldulcitol (VI).

EXPERIMENTAL

1,6-Diacetyl-dicyclohexylidene-dulcitol (II). 6.5 ml acetic anhydride was added to a solution of 1.71 g dicyclohexylidene-dulcitol (m.p. 142°) in 10 ml anhydrous pyridine. A slight evolution of heat was observed. The mixture was left to stand for 24 hours, after which 60 ml ice water was added and crystallization began. The precipitate was filtered off, washed thoroughly with water and dried. Yield 2.06 g (96.7%). M. p. 97.5-98° after recrystallization from alcohol.

Found %: C 61.95, 61.69; H 7.86, 8.05. $C_{22}H_{34}O_8$. Calculated %: C 61.97; H 7.98.

1,6-Diacetyldulcitol (VI, R = $COCH_3$). 1 g diacetyl-dicyclohexylidene-dulcitol (m.p. 97-98°) was dissolved in 20 ml glacial acetic acid and 4 ml water added. The mixture was heated for 2 hours on the water bath, a further 6 ml of water added and heating continued for a further hour. The solvent was removed under reduced pressure, the solid residue dissolved by heating in 10 ml anhydrous alcohol and the alcohol evaporated at room temperature. Recrystallization yielded 0.1 g substance with m.p. 166-167° [5, 8].

1,6-Dibenzoyl-dicyclohexylidene-dulcitol (III). Benzoylchloride (1.75 g) was added in small portions at 0° to a cooled solution of 1.71 g dicyclohexylidene-dulcitol (m.p. 142°) in 13 ml anhydrous pyridine; after a short time the solution became turbid and a precipitate came down. The reaction mixture was left to stand for twenty-four hours at room temperature. Ice water was then added and crystallization began. The precipitate was filtered off and washed in turn with water, 3% hydrochloric acid, 5% sodium carbonate solution and water, and then dried. Yield 2.48 g (89.6%). Recrystallized from a mixture of alcohol and benzene; glistening plates with m.p. 157-158°. Soluble in benzene at room temperature, soluble with difficulty in alcohol.

Found %: C 70.01; H 7.00. M 542. $C_{32}H_{38}O_8$. Calculated %: C 69.81; H 6.91. M 550.

1,6-Dibenzoyldulcitol (VI, R = COC_6H_5). 1 g 1,6-dibenzoyl-2,3 : 4,5-dicyclohexylidene-dulcitol and 50 ml 80% acetic acid were heated on the water bath for 3 hours; 10 ml water was then added and heating continued for a further 2 hours. The solvent was removed under reduced pressure and the dry residue washed with 10 ml hot anhydrous alcohol. This yielded 0.26 g of substance in the form of thin colorless plates with m.p. 208-209° (from glacial CH_3COOH) [5, 8].

The oxidation of dicyclohexylidene-dulcitol (I) with lead tetraacetate. 1.7 g dicyclohexylidene-dulcitol (m.p. 142°), 50 ml glacial acetic acid and 2.6 g lead tetraacetate (theoretical quantity 2.4 g) were heated with stirring to 40-45°. Samples taken for analysis at intervals of $^1/_2$, 1, 2, 3 and 4 hours showed that the lead tetraacetate had not reacted.

1,6-Ditosyl-dicyclohexylidene-dulcitol (IV). 30 g toluenesulfonyl chloride was added in small portions to a solution of 17.1 g dicyclohexylidene-dulcitol in 60 ml anhydrous pyridine. The mixture was left to stand for 8 days at room temperature and a thick mass formed. Ice water was added dropwise until a turbidity appeared, crystallization began, the mixture was shaken, the precipitate filtered off, washed with 3% HCl and then with water, filtered off and dried. Yield 28.5 g (86%); m.p. 133-135° (from acetone).

Found %: S 9.47, 9.49. $C_{32}H_{42}O_{10}S_2$. Calculated %: S 9.80.

1,6-Ditrityl-dicyclohexylidene-dulcitol (V). 0.85 g dicyclohexylidene-dulcitol (m.p. 142°) was added to a solution of 1.61 g trityl chloride (triphenylmethyl chloride) in 15 ml anhydrous pyridine. The mixture was left to stand for 5 days. Crystallization began after ice had been added. The precipitate was filtered off, washed thoroughly with water and dried: weight 2.26 g (contains traces of triphenylcarbinol). The product was treated with acetone and then with ether and recrystallized from carbon tetrachloride. Yield 0.87 g (32.83%), m.p. 240°.

It does not dissolve in alcohol, ether, acetone; dissolves with heating in carbon tetrachloride.

Found %: C 81.00; H 7.14. $C_{56}H_{58}O_6$. Calculated %: C 81.35; H 7.02.

SUMMARY

1. It has been shown that the hydrolysis of dibenzoyl-dicyclohexylidene-dulcitol and diacetyl-dicyclohexylidene-dulcitol yields 1,6-dibenzoyldulcitol and 1,6-diacetyldulcitol.

2. The following crystalline compounds, which are not described in the literature, have been synthesized: 1,6-diacetyl-dicyclohexylidene-dulcitol, 1,6-dibenzoyl-dicyclohexylidene-dulcitol, 1,6-ditosyl-dicyclohexylidene-dulcitol and 1,6-ditrityl-dicyclohexylidene-dulcitol (1,6-triphenylmethyl-dicyclohexylidene-dulcitol).

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THE STRUCTURE AND REACTIVITY OF PIASELENOLE

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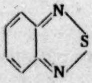
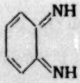
A study has already been made of the reactivity of piazothiole, which is an example of a substance in which the powerfully electrophilic thiodiazole ring causes a breakdown of the bond regularity in the condensed benzene ring with the formation of the quinoid structure (I) [1, 2]. It was noted that this compound exhibits aromatic character and does not show the tendency to undergo addition reactions which is typical of substances with a quinoid structure.

An explanation of this may be found in a comparison of the structure of piazothiole (I) with that of, for example, o-quinonediimine (II).



(I)

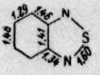


(II)

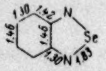
In o-quinonediimine (II) the nitrogen atoms are the polar extremities of conjugated bond systems. In piazothiole (I) however, these ends are closed into a ring system by a sulfur atom, which has a powerful affinity for electrons. Under the influence of this atom, electrons are drawn off from the bond system of the benzene ring of piazothiole and this hinders the course of the addition reaction.

In this connection it was considered of interest to study a compound of analogous structure to piazothiole, but with a ring-closing hetero-atom of lower electronegativity.

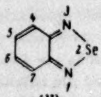
As an example of such a compound for study, the substance chosen was piaselenole (V) which exhibits a breakdown in the bond regularity in the benzene ring which is similar to that in piazothiole (I). Below, for comparison, are given the interatomic distances in the molecules of both compounds found by Luzzati [3].



(III)



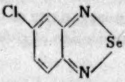
(IV)



(V)

Piaselenole, first described by O. Hinsberg [4], is formed in quantitative yield by mixing aqueous solutions of selenium dioxide and o-phenylenediamine. Attention is drawn to the extreme ease with which this reaction takes place in comparison with the reaction by which piazothiole is formed, which takes place only in fairly severe conditions. We explain the ease of this reaction by the mechanism of condensation of the o-diamine with selenium dioxide. The conversion of the o-diamine into piaselenole appears to us to involve the oxidation of the diamine by selenium dioxide to a derivative of o-quinonediimine (II) with conversion of the latter into piaselenone. The ease of formation of piaselenole, compared with piazothiole, is thus dependent on the oxidizing power of selenium dioxide, which is considerably greater than that of sulfur dioxide.

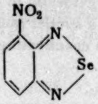
Proof of this sequence of changes might be obtained by carrying out the condensation in conditions in which the intermediate derivative of o-quinonediimine (II) would, for example, add on the elements of a hydrogen halide to its conjugated double bond system. Indeed, by carrying out the condensation of o-phenylenediamine with selenium dioxide in concentrated hydrochloric acid, we obtained 5-chloropiaselenole (VI), whose structure was confirmed by the alternative synthesis from 4-chloro-1,2-phenylenediamine.

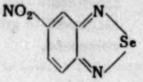

(VI)

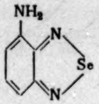
3,4-Toluylenediamine evidently reacts in analogous fashion with selenium dioxide in concentrated hydrochloric acid [5].

At the same time, attempts to add on hydrogen chloride to piaselenole itself under different conditions, including tests in the presence of a number of catalysts, invariably led only to the formation of its hydrochloride.

The behavior of piaselenole in substitution reactions shows its full analogy with piazothiole. Thus the nitration of piaselenole, which takes place fairly readily in concentrated sulfuric acid with a slight excess of nitrating mixture, gives 4-nitropiaselenole (VII). The structure of this product was proved by comparing it with the isomeric 4-nitro- and 5-nitropiaselenoles (VII, VIII) prepared by an alternative synthesis. On the other hand, we were able to reduce the nitration product (VII) to 4-amino-piaselenole (IX), which we also synthesized from triaminobenzene.


(VII)


(VIII)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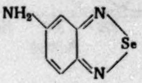

(X)

In the same way we prepared the isomeric 5-aminopiaselenole (X), described earlier by Hinsberg [4].

It should be noted that, in the reaction of selenium dioxide with triaminobenzene, even a slight excess of the former leads to the irreversible oxidation of the aminopiaselenole formed. It is therefore much better to use the aminobenzene in the form of its hydrochloride, and to use sodium selenite instead of selenium dioxide.

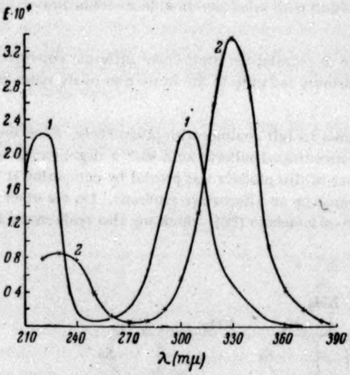
Both amines form needles of an intense reddish-yellow color; 5-aminopiaselenole, unlike the 4-isomer, is readily soluble in water and is much more readily oxidized. Both amines are very weak bases: the dissociation constants of the bases, calculated from potentiometric titration data (see experimental part) is equal to $10^{-10.8}$ for both products. The intensity of the color and the low basic strength of the amines provides evidence for the quinoid structure of the piaselenole molecule.

At the same time the color of these compounds is deeper, and the basic dissociation constants are somewhat higher, than those of the corresponding amines of piazothiole ($10^{-11.3}$) [2]. This confirms our suggestion that, as a result of the lower electronegativity of the selenium in piaselenole, a reduced regularity of the bonds in the heterocyclic ring is to be expected. Further evidence for this is provided by a comparison of the dipole moments of piazothiole and piaselenole found by Hill and Sutton [6] and of the half-wave potentials (reduction potentials) of these compounds found by us (Table).

Product studied	Dipole moment D	Reduction potential (in
Piazothiole	1.73	−1.7
Piaselenole	0.94	−1.1

Piaselenole, as a result of the lower electronegativity of the selenium, is a less polar compound. According to the law of Shikata and Tachi [7], the introduction of groups of lower electronegativity into a compound results in a lowering of its reduction potential.

A comparison of the absorption spectra of piaselenole and piazothiole also shows clearly a shift of the absorption maxima of piaselenole towards the long wave region (Figure).



Absorption spectra.
1) piazothiole, 2) piaselenole.

All these data provide evidence for the greater quinoid structure of piaselenole in comparison with piazothiole and in this sense confirm our original suggestions. Nevertheless, attempts to add maleic anhydride to piaselenole (and to piazothiole), as well as attempts to add divinyl to piaselenole, which we carried out using extreme conditions, were unsuccessful. In all the experiments we recovered the original materials almost quantitatively.

This inability of piaselenole, and of piazothiole, to undergo addition reactions corresponds, for example, with the deactivation of butadiene-1,3 when a nitro group – a powerfully electrophilic substitutuent – is introduced into the molecule [8]. Evidently in our case the seleno- and thiodiazole ring is a similar (and perhaps even stronger) electrophilic group deactivating the double bond of the compound.

EXPERIMENTAL

The preparation of 5-chloropiaselenole. 3 g o-phenylenediamine was mixed with 50 ml concentrated hydrochloric acid and a solution of 3.08 g selenium dioxide in 20 ml concentrated hydrochloric acid added; reaction took place with appreciable evolution of heat. When cooled, the reaction mass yielded 3.5 g of a brown precipitate with the odor of quinoxaline characteristic of piaselenoles. The product was washed and steam distilled to yield 1.2g of the chloro derivative in the form of silvery-white plates. M.p. 114-115° (with sublimation). The product was crystallized from aqueous alcohol. White needles were obtained, which began to sublime in a capillary at 114° and melted within the range 117.5-118°. The product is soluble in alcohol, ether and acetone. Sparingly soluble in water.

As a proof of its structure, the same product was synthesized from 4-chloro-1,2-phenylenediamine. An aqueous solution of 1.28 g selenium dioxide was added with stirring to an aqueous solution of 1.65 g of 4-chloro-1,2-phenylenediamine dihydrochloride. In the process the solutions formed a paste of fine white needles. The mass was filtered and the residue obtained dried in an oven at 90°. 1.6 g of dry chloropiaselenole was obtained. The product was purified in aqueous alcohol with activated charcoal and crystallized in the form of white needles. In a capillary the product began to sublime at 115° and melted at 117-118°. A mixed sample of both products melted at the same temperature.

Found %: N 12.93, 12.85; Cl 16.08. $C_6H_3ClN_2Se$. Calculated %: N 12.87; Cl 16.32.

Attempts to add hydrogen chloride to paiselenole were made using different conditions; for example, in solution in carbon tetrachloride and dioxane in the presence of oxidizing catalysts (nitrobenzene, selenium dioxide, etc.) and in their absence, in concentrated hydrochloric acid. In all cases the only product isolated had m.p. 159-160°, contained ionic chloride, and proved to be piaselenole hydrochloride.

Found %: HCl 16.42, 16.30. $C_6H_4N_2Se \cdot HCl$. Calculated %: HCl 16.63.

The nitration of piaselenole. 1.2 g piaselenole and 10 ml concentrated sulfuric acid were placed in a two-necked flask fitted with mechanical stirrer and stirred thoroughly with cooling by ice and salt until the piaselenole had completely dissolved. A mixture of 1.8 ml nitric acid (d 1.4) and 2.7 ml sulfuric acid (d 1.84) was poured from the dropping funnel into the flask, with uninterrupted stirring and cooling. The mass was stirred for a further 30 minutes and then poured on to ice. Pale yellow crystals of the nitro derivative separated immediately. The mixture was filtered and the residue washed with water until no longer acid to congo red. Yield of nitro derivative 1.47 g (98.5%). M.p. 210° (with sublimation). The product was purified with activated charcoal and crystallized from alcohol. The pure product had m.p. 216.5-217.5° (with sublimation). Readily soluble in alcohol and benzene.

For proof of the structure of the nitration product it was compared with 4-nitro- and 5-nitropiaselenoles prepared from the corresponding nitro-1,2-phenylenediamines. A mixture of 40 ml water and 2.17 g of finely divided diamine (or a solution of it in dilute hydrochloric acid) was placed in a two-necked flask fitted with stirrer and an aqueous solution of 1.48 g selenium dioxide added slowly dropwise with stirring. The red color of the mass gradually changed to pale yellow. When the color change was complete the reaction mass was stirred for a further short time and then filtered to isolate the product.

In this way 3.12 g (98%) of 5-nitropiaselenole was obtained from 2.23 g 4-nitro-1,2-phenylenediamine. The product, recrystallized from alcohol, melted at 220-220.5° (with sublimation). It dissolves in benzene, acetone and glacial acetic acid; its solubility in alcohol is considerably lower than that of 4-nitropiaselenole. It sublimes much more readily than the latter. Under the microscope it appears as rhombic crystals. A specimen of a mixture with the product of the nitration of piaselenole gave a depression (209-212°).

Found %: N 18.30, 18.41. $C_6H_3N_3O_2Se$. Calculated %: N 18.42.

In the conditions described above, 3-nitro-1,2-phenylenediamine was converted quantitatively into 4-nitropiaselenole. It crystallized from alcohol in the form of beveled parallelepipeds (under the microscope). M.p. 217-217.5° (with sublimation). A specimen of a mixture with the product of the nitration of piaselenole at the same temperature.

Found %: N 18.28, 18.74. $C_6H_3N_3O_2Se$. Calculated %: N 18.42.

The preparation of 4-aminopiaselenole. a) The reduction of 4-nitropiaselenole. 12 g iron turnings and 100 ml water were placed in a two-necked flask fitted with reflux condenser and stirrer. The stirrer was switched on and the mixture heated to boiling on the water bath. 2 ml 98% acetic acid was added to the boiling liquid, followed after a short interval by 3.8 g 4-nitropiaselenole. The mixture was boiled for half an hour. The hot reddish-brown reaction mass was filtered from the sludge. The sludge was carefully washed with hot water (100-150 ml) and the wash waters added to the main filtrate. The turbid brown filtrate, which had a strong amine-like odor, yielded cherry-red crystals of the amine on slight cooling. The mass was cooled thoroughly and the precipitated amine separated. It was then dissolved in moderately concentrated hydrochloric acid, the solution was filtered, the filtrate cooled and neutralized with ammonia. Yellow-red flakes of the amine separated and were filtered off and dried in a vacuum desiccator. Yield 1.65 g (52%). M.p. 151-152°. When 0.6 g selenium dioxide was added to the filtrate obtained on separation of the amine from the reduced solution, a further 0.9 g of 4-aminopiaselenole could be obtained. Total yield 2.55 g (81%). Recrystallization from water after activated charcoal treatment yielded very long reddish-yellow needles with m.p. 159-159.8°.

b) The condensation of 1,2,3-triaminobenzene with selenium dioxide. Aqueous solutions of 14 g 1,2,3-triaminobenzene and 13.9 g sodium selenite were mixed and very pure 4-aminopiaselenole with m.p. 159-160° was obtained in quantitative yield. The product was fairly readily soluble in hot water and quite sparingly soluble in cold. On prolonged standing its aqueous solutions were oxidized and dark flakes separated. It is readily soluble in organic solvents. In concentrated hydrochloric acid it gave a grey precipitate of the salt, which is very readily hydrolyzed.

Found %: N 21.25, 21.15. $C_6H_5N_3Se$. Calculated %: N 21.20.

The basic dissociation constant of 4-aminopiaselenole was determined by potentiometric titration in aqueous alcohol (3 : 1) at 20° to the pH of the half-neutralization point, using a valve potentiometer LP-4 and glass electrode.

0.0319, 0.0306 g substance: pH of the half-neutralization point 3.185, 3.196.

The preparation of 5-aminopiaselenole. a) The reduction of 5-nitropiaselenole using the conditions employed for 4-nitropiaselenole, i.e. with iron in acid solution, led to the formation of a tarry precipitate which could not be purified. Attempts to reduce 5-nitropiaselenole with iron in neutral solution were unsuccessful. It was not possible either to separate the amine in the form of its acetyl derivative.

b) The condensation of 1,2,4-triaminobenzene dihydrochloride with sodium selenite was carried out as in the experiment with 1,2,3-triaminobenzene. 5-Aminopiaselenole was obtained in quantitative yield. M.p. 148°. The product was treated with activated charcoal and crystallized from water in the form of fine reddish-yellow needles. M.p. 149-150°.

5-Aminopiaselenole is considerably more soluble in hot and in cold water than the 4-isomer; it is soluble in organic solvents. It is very readily oxidized in air. On standing in air its solutions yield a black precipitate after only an hour. In concentrated hydrochloric acid it gives a red salt which is very easily hydrolyzed.

The basic dissociation constant of 5-aminopiaselenole was determined by potentiometric titration in aqueous alcohol solution at 21° to the pH of the half-neutralization point, using a valve potentiometer LP-4 and glass electrode.

0.0507, 0.0504 g substance: pH of the half-neutralization point 3.033, 3.015.

Attempts to add maleic anhydride to piaselenole. A toluene solution of piaselenole and freshly distilled maleic anhydride was kept for 3 hours on a boiling water bath and at 150° in a sealed tube. When a twofold excess of 10% alkali was added to the reaction mixture, the original materials were recovered almost quantitatively.

Experiments were carried out with piazothiole in analogous conditions and with similar results.

Attempts to add piaselenole to butadiene-1,3. Piaselenole dissolved in xylene was heated with divinyl in a sealed tube at 140 and 200° for 4 hours. Unchanged piaselenole was recovered from the reaction mass after distillation of the xylene.

Spectroscopy. The absorption spectra of piaselenole and piazothiole were recorded using a spectrophotometer SF-4.

Measurements were carried out every 10 mμ within the range of wavelengths from 215-400 mμ.

Polarography. The half-wave potential (V dropping mercury electrode, tangential method) was recorded on a standard polarograph of the Heyrovsky-Shikata type at 20° in an alcoholic acetate buffer. Concentration of substance 10^{-4} M.

SUMMARY

1. The conversion of o-phenylenediamine to piaselenole takes place apparently with the intermediate formation of a derivative of o-quinonediamine.

2. A comparison of the basic dissociation constants of the isomeric 4- and 5-aminopiaselenoles and the corresponding aminopiazothioles, together with a comparison of the reduction potentials, dipole moments and position of the maxima on the absorption spectra of piaselenole and piazothiole, shows that the quinoid structure is more marked in piaselenole than in piazothiole.

Nevertheless, the characteristic reactions of piaselenole, as of piazothiole, are those of substitution and not of addition.

3. The inability of these two compounds to undergo addition reactions is explained by the deactivating influence of the powerfully electrophilic seleno- or thiodiazole ring on the bond system in the condensed benzene ring.

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THE PROBLEM OF INDICATOR CHANGES

O. F. Ginzburg and B. A. Porai-Koshits

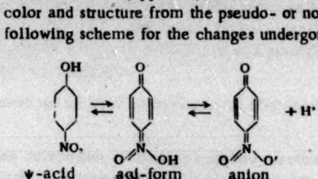
As early as the eighteen-nineties, Ostwald, as is well known, concluded, from a generalization of the results of a study on the color of ionic solutions in the light of the theory of electrolytic dissociation, that acid-base indicators are weak bases or acids whose ionization is accompanied by the formation of ions with a different visible color from the undissociated molecules [1]. Consequently, in accordance with the theory of protolytic equilibrium, systems in which the conjugate acids and bases have different colors are indicators [2].

During the 60 years and more which have passed since the appearance of Ostwald's works on indicators, there has accumulated a great deal of experimental material related to the properties and changes of the latter, which has confirmed the accuracy of Ostwald's theories on indicators and weak electrolytes.

As is well known, the processes of ionization and its reversal, which are connected with the rupture or formation of covalent bonds, lead to the appearance or disappearance of electron-donating or electron-accepting groupings, as a result of which the nature of the conjugated systems in the molecules and the ions formed from them are different. Since indicators are compounds with a covalent structure, the structure of the indicator molecules is essentially different from the structure of the ions formed from them, as a result of which the light absorption of the ions and the molecules is different.

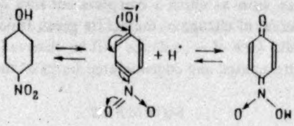
Almost simultaneously with the appearance of Ostwald's theory of indicators, Hantzsch put forward a theory that substances with a non-ionic structure, whose solutions contain ions, form a special group of non-electrolytes, called by the author "pseudo-electrolytes" [3, 4]. Hantzsch suggested that "pseudo-electrolytes" are capable of isomerizing in solution to electrolytes which then dissociate into ions; Hantzsch, however, did not explain the mechanism of the proposed isomerization.

At the present time, as is well known, compounds, with either ionic or covalent structure, whose solutions contain ions, are classed as electrolytes. In this connection the ability of a compound to act as an electrolyte depends not only on its chemical structure but also on the nature of the solvent. Thus the same compounds in different solvents may form, with one, solutions which do not conduct electricity and, with another, may behave as weak or even strong electrolytes. Inasmuch as the rupture of a covalent bond, brought about by the interaction of the dissolved substance with the solvent, leads first of all to the formation of ions, it must be admitted that Hantzsch's theory of "pseudo-electrolytes" is without sense. It should be noted that towards the end of the nineteen-twenties Hantzsch himself came partly to the same conclusion [5]. Nevertheless, the ideas of "pseudo-electrolytes," "pseudo-acids," "pseudo-bases" and "pseudo-salts" are still being used for the explanation of a whose series of phenomena [6], including the characteristics of the mechanism of indicator changes [7-9]. Thus, for example, Kolthoff has written: "indicators are (apparent) weak acids or bases, whose ionic or acidic (or basic, respectively) form has a different color and structure from the pseudo- or normal compound" [10, 11]. In accordance with this, Kolthoff gives the following scheme for the changes undergone by p-nitrophenol



The change in color of p-nitrophenol solution is thus related by the supporters of the Hantzsch theory to the transformation of the colorless pseudo-acid to the yellow colored acidic or aci-form, which by undergoing ionization forms an anion which, like the undissociated aci-form, has a yellow color.

If it is assumed that p-nitrophenol exists in two tautomeric forms, then the tautomeric change of p-nitrophenol, which, like all other prototropic tautomeric changes, takes place by an ionic mechanism, should be expressed by the following scheme



i.e. the stage involving the dissociation of the phenolic form precedes the formation of the quinoid form, while this process is reversible. The color of the solution is thus due to the color of the organic anion, in which the distribution of electron density is substantially different from the electron density distribution in the undissociated p-nitrophenol.

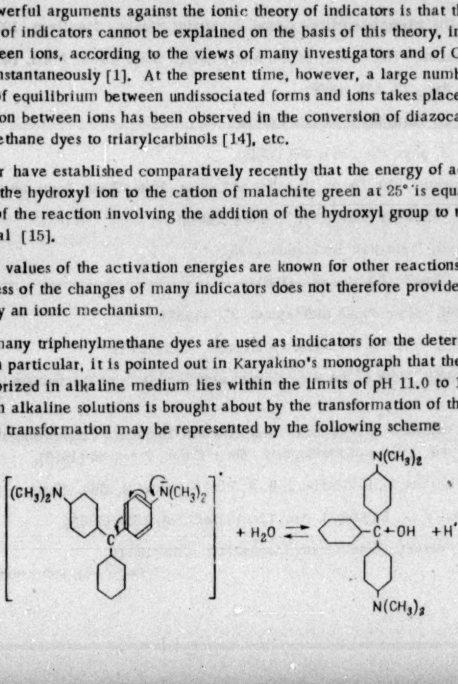
From the structural characteristics of the quinoid form of p-nitrophenol it may be taken that it should be a much weaker acid than the phenolic form. As M. I. Kabachnik has shown, "the ionization constant of an equilibrium tautomeric mixture is of similar magnitude to the ionization constant of the less acidic form in a given medium" [12]. The constant obtained as a result of the study of the acid-base equilibrium in a solution of p-nitrophenol must therefore be taken as characterizing the ionization of the phenolic form of the p-nitrophenol. It is therefore incorrect to describe as "apparent" or "virtual" the experimentally determined ionization constants of p-nitrophenol and other indicators which may also be classified as tautomeric compounds [8, 10].

One of the most powerful arguments against the ionic theory of indicators is that the slow character of the changes of a whole series of indicators cannot be explained on the basis of this theory, inasmuch as the attainment of equilibrium between ions, according to the views of many investigators and of Ostwald himself in particular, takes place almost instantaneously [1]. At the present time, however, a large number of changes are known in which the attainment of equilibrium between undissociated forms and ions takes place slowly. Thus, for example, a slow interaction between ions has been observed in the conversion of diazocations to diazohydrates [13], of the cations of triarylmethane dyes to triarylcarbinols [14], etc.

Turgeon and La Mer have established comparatively recently that the energy of activation of the reaction involving the addition of the hydroxyl ion to the cation of malachite green at 25° is equal to 14.4 kcal, while the energy of activation of the reaction involving the addition of the hydroxyl group to the cation of crystal violet is equal to 15.1 kcal [15].

At the present time values of the activation energies are known for other reactions taking place between ions [16, 17]. The slowness of the changes of many indicators does not therefore provide evidence that these changes do not proceed by an ionic mechanism.

As is well known, many triphenylmethane dyes are used as indicators for the determination of pH in acid and alkaline solutions. In particular, it is pointed out in Karyakino's monograph that the interval over which malachite green is decolorized in alkaline medium lies within the limits of pH 11.0 to 13.5 [8]. The decolorization of malachite green in alkaline solutions is brought about by the transformation of the dye to the colorless carbinol compound. This transformation may be represented by the following scheme



and this reaction may take place slowly. In recent years the magnitude of the hydrolysis constant of malachite green has been established and this, according to the data from many investigators, has proved to be close to 10^{-7} [18-20]. In this case therefore, there is no direct relationship between the ionization constant of the indicator and the interval over which it changes. In this connection it should be noted that in solutions whose pH differs by only 1-2 units from the value of pK_h for malachite green, the rate of hydrolysis and consequently the rate of decolorization of solutions of the latter is comparatively small. In solutions with a higher concentration of hydroxyl ions, the decolorization of malachite green may take place very rapidly. In the titration of an acid solution with alkali in the presence of malachite green as indicator, therefore, the change in color of the solutions is observed at higher pH values than those at which a complete but slow decolorization of the solution is possible. This explains the fact that the interval of change of malachite green is not in accordance with its hydrolysis constant. It should be noted that this lack of accordance will be observed in all those cases where the equilibrium in the solution between the dissociated and undissociated forms of the indicators is established slowly.

SUMMARY

1. The theory of "pseudo-electrolytes" put forward by Hantzsch does not stand strict criticism in the light of contemporary ideas on the process of ionization and its reversal.

2. Ostwald's theory that indicators are weak acids and bases whose ions have a different visible color from the undissociated molecules, which has been rejected by many investigators, is correct. In this connection it must be borne in mind, however, that for a number of indicators the attainment of equilibrium between the dissociated and undissociated forms may take place slowly.

3. If an indicator exists in two tautomeric forms, then the so-called "virtual" or "apparent" ionization constant of the indicator characterizes its less ionizing form.

4. In choosing an indicator it is necessary to take into consideration not only its ionization constant but also the rate of attainment of equilibrium between the dissociated and undissociated forms of the indicator.

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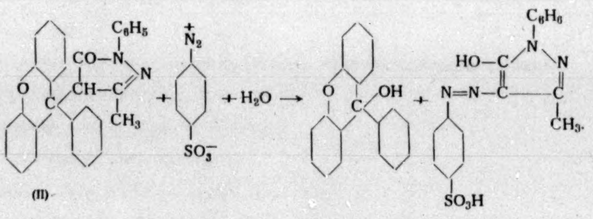
THE PRODUCTS OF THE CONDENSATION OF ARYLCARBINOLS WITH 1-PHENYL-3-METHYLPYRAZOLONE-5. III

O. F. Ginzburg, Ts. M. Goldberg and E. I. Kvyat

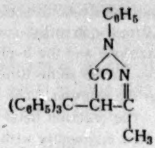
In a previous communication [1] it was pointed out that 9-phenyl-9-hydroxy-10-methyl-9,10-dihydroacridine in methyl alcohol reacts with 1-phenyl-3-methylpyrazolone-5 with the formation of 1-phenyl-3-methyl-4-(9'-phenyl-10'-methyl-9',10'-dihydroacridyl-9')-pyrazolone-5 (I).

Further experiments, described in the present communication, have shown that in analogous conditions condensation of 1-phenyl-3-methylpyrazolone-5 with 9-phenylxanthydrol also takes place. The 9-phenyl-9-(1'-phenyl-3'-methyl-4',5'-dihydro-5'-oxo-4'-pyrazolyl)-xanthene (II) thus formed proved to be a much more stable substance than compound (I). Thus, for example, compound (II), unlike compound (I), is not decomposed by glacial acetic acid. Compound (II) may therefore also be prepared in quantitative yield by heating an equimolecular mixture of 9-phenylxanthydrol and 1-phenyl-3-methylpyrazolone-5 in glacial acetic acid.

Compound (II), like the products of the condensation of arylcarbinols with 1-phenyl-3-methylpyrazolone-5 prepared earlier, dissolves in aqueous alcohol solutions of alkali without undergoing decomposition in the process. When diazosulfanilic acid is added to the alkaline aqueous alcohol solution of compound (II), this compound is split up.



In the process, the pyrazolone azo-dye remains in solution while the 9-phenylxanthydrol is precipitated. Since the azo-coupling reaction takes place in aqueous alcohol solution, it is not impossible that a certain amount of the ethyl ester of 9-phenylxanthydrol is formed together with the latter compound. In alkaline aqueous alcohol solutions, diazosulfanilic acid reacts in analogous fashion with compound (I), 1-phenyl-3-methyl-4-triphenylmethylpyrazolone-5 (III), bisphenyl-p-dimethylaminophenyl-(1-phenyl-3-methyl-4,5-dihydro-5-oxo-4-pyrazolyl)-methane (IV) and bis-(p-dimethylaminophenyl)-phenyl-(1-phenyl-3-methyl-4,5-dihydro-5-oxo-4-pyrazolyl)-methane (V).



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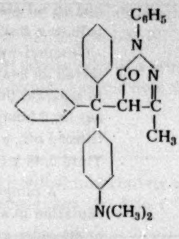

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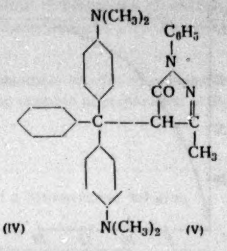
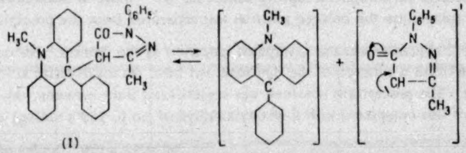


(V)

Thus the decomposition of the products of the condensation of arylcarbinols with 1-phenyl-3-methylpyrazolone-5 takes place not only in acetic acid [1] but also in alkaline aqueous alcohol solutions.

Several years ago it was shown, on the basis of spectrophotometric measurements, that, in nitrobenzene, compound (V) is able to undergo dissociation, which takes place slowly at room temperature and is accompanied by rupture of the bond between carbon atom 4 of the pyrazolone ring and the arylcarbinol residue [2]. Since ions are formed as a result of this dissociation, it was to be expected that together with the spontaneous increase in the intensity of color of freshly-prepared nitrobenzene solutions of compound (V) there should also be observed a spontaneous increase in the electrical conductivity of such solutions. The experiments carried out confirmed the existence of a parallelism of this nature. Thus, for example, the electrical conductivity of a nitrobenzene solution of compound (V)(about 10^{-2} M) at a temperature of 25° reached a maximum value only several hours after the preparation of the solution.

In the previous communication it was pointed out that compound (I), like compound (V), undergoes dissociation in various solvents, including nitrobenzene, and this dissociation may be represented by the following equation



(I)

As we wished to follow the course of the dissociation of compound (I), we made a study of the electrical conductivity of solutions of this compound. Figure 1 shows the curve characterizing the spontaneous change in the electrical conductivity of a nitrobenzene solution of compound (I). Examination of the diagram shows that the increase in the electrical conductivity of the solution of compound (I) takes place over a period of several days. Thus in nitrobenzene solutions at room temperature the process of dissociation of compound (I) takes place slowly.

EXPERIMENTAL

9-Phenyl-9-(1'-phenyl-3'-methyl-4',5'-dihydro-5'-oxo-4'-pyrazolyl)-xanthene (II). a) 0.40 g 9-phenylxanthydrol ($1.4 \cdot 10^{-3}$ mole) was added to a solution of 0.30 g 1-phenyl-3-methylpyrazolone-5 ($1.7 \cdot 10^{-3}$ mole) in 20 ml anhydrous methyl alcohol and the mixture obtained boiled on a water bath in a flask fitted with reflux condenser. The 9-phenylxanthydrol dissolved on heating and the solution acquired a yellow color. After some time a precipitate began to separate from the solution. The heating was carried out for 2 hours. The reaction mass was cooled, the residue filtered off, washed thoroughly with methyl alcohol and dried. Yield 0.60 g (95.8% calculated on the 9-phenylxanthydrol) with m.p. 220-221°.

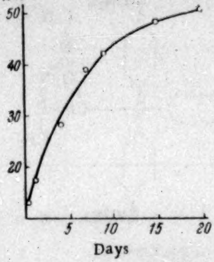


Fig. 1. The change in the electrical conductivity of a nitrobenzene solution of compound(I). (about 10^{-2} M, temperature 25± ± 0.05°).

b) 0.20 g 1-phenyl-3-methylpyrazolone-5 ($1.10 \cdot 10^{-3}$ mole), 0.30 g 9-phenylxanthydrol ($1.1 \cdot 10^{-3}$ mole) and 10 ml glacial acetic acid were heated on a water bath in a flask fitted with reflux condenser. The 1-phenyl-3-methyl-pyrazolone and the 9-phenylxanthydrol dissolved on heating. After some time a precipitate began to separate from the solution. The heating was carried out for 2 hours. The reaction mass was cooled, the residue filtered off, washed thoroughly with alcohol and dried. Yield 0.45 g (95.6%) of substance with m.p. 220-221°.

A sample of the mixed products obtained by condensation in alcoholic and in acetic acid solutions melted at the same temperature.

Found %: N 6.53, 6.56. $C_{29}H_{22}O_2N_2$. Calculated %: N 6.52.

c) 0.6 g of caustic soda was dissolved in 20 ml 60% aqueous alcohol. 0.10 g of compound (II) was added to the solution obtained. The compound dissolved completely. The solution obtained was boiled for 3 hours in a flask fitted with reflux condenser. The solution was cooled and acidified with acetic acid. Compound (II) was recovered quantitatively from the solution.

d) 0.10 g of compound (II) was dissolved with heating in 5 ml of glacial acetic acid and one drop of concentrated hydrochloric acid added to the solution obtained. The solution was heated for 3 hours in a flask fitted with reflux condenser at 155-160°. The acetic acid solution was then poured into water. The original compound separated quantitatively.

The action of diazo-compounds on the products of the condensation of arylcarbinols with 1-phenyl-3-methylpyrazolone-5. a) 0.43 g (10^{-3} mole) of compound (II) was added to a solution of 1.00 g caustic soda in 10 ml 60% ethyl alcohol and the compound rapidly dissolved. 10^{-3} mole of diazosulfanilic acid was added to the solution formed. After some time the colored solution was separated from the precipitate obtained.

Curve 1 in Figure 2 characterizes the absorption spectrum of the filtrate. For comparison the same Figure shows the absorption curve for a solution of the dye obtained from diazosulfanilic acid and 1-phenyl-3-methylpyrazolone-5 (Curve 2). The precipitate obtained was crystallized from benzene. M.p. after two recrystallizations 159°. A mixture of this compound with 9-phenylxanthydrol (m.p. 159°) melted at the same temperature.

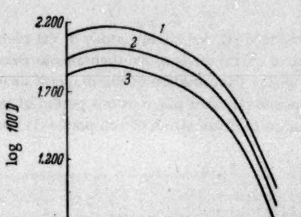


Fig. 2. Absorption spectra of the dyes obtained by the action of diazosulfanilic acid on the products of the condensation of arylcarbinols with 1-phenyl-3-methylpyrazolone-5. Explanation in the text.

b) 0.42 g (10^{-3} mole) of compound (III) was dissolved in 10 ml of an aqueous alcohol solution of alkali prepared as described above. 10^{-3} mole of diazosulfanilic acid was added to the solution obtained. The solution slowly acquired an orange-red color. After some time the precipitate which formed was filtered off. Curve 3 in Fig. 2 characterizes the absorption spectrum of the filtrate. The precipitate obtained was recrystallized from benzene. M.p. 162° after two recrystallizations. A mixture of the compound obtained with triphenylcarbinol (m.p. 162°) melted at the same temperature.

The reaction of diazosulfanilic acid with compounds (I), (IV) and (V) was carried out under analogous conditions. The absorption spectrum of the dyes thus obtained proved to be identical with the absorption spectrum of the dye obtained from diazosulfanilic acid and 1-phenyl-3-methylpyrazolone-5.

The study of the electrical conductivity of nitrobenzene solutions of compounds (I) and (V). The constant k of the instrument used for the measurement of the electrical conductivity was 0.117. The specific conductivity of the nitrobenzene varied within the limits $1.6 \cdot 10^{-7}$ to $1.8 \cdot 10^{-7}$.

a) The measurement of the electrical conductivity of a nitrobenzene solution of compound (V) (about 10^{-2} M) was carried out at definite time intervals, counted from the moment of preparation of the solution. The values obtained are given in Table 1.

TABLE 1

The Change in the Electrical Conductivity of a Nitrobenzene Solution of Compound (V) (temperature 25 ± 0.05°)

Time (hours)	$\varkappa \cdot 10^6$	λ
2	8.8	0.88
24	20.2	2.02
72	20.2	2.02

b) A solution of 10^{-2} M concentration was prepared by dissolving compound (I) in nitrobenzene and the change in the electrical conductivity of this solution followed over a period of 15 days. The solution was then diluted 5 times (about $2 \cdot 10^{-3}$ M) and the solution thus obtained diluted again 5 times after 15 days (about $4 \cdot 10^{-4}$M). The measurement of the electrical conductivity of the solutions was carried out at definite time intervals, counted from the moment of preparation of a solution of a given concentration. The values obtained are given in Table 2.

TABLE 2

The Change in the Electrical Conductivity of Nitrobenzene Solutions of Compound (I) (temperature 25 ± 0.05°)

Time (days)	c $1 \cdot 10^{-2}$ M.		c $2 \cdot 10^{-3}$ M.		c $4 \cdot 10^{-4}$ M.	
	$\varkappa \cdot 10^6$	λ	$\varkappa \cdot 10^6$	λ	$\varkappa \cdot 10^6$	λ
0.1	13.1	1.31	16.0	8.1	3.24	8.1
1	17.7	1.77	16.4	8.2	3.56	8.9
4	28.4	2.84	16.8	8.4	3.70	9.2
7	39	3.9	17.0	8.5	4.00	10.0
9	43	4.3	—	—	—	—
15	48	4.8	17.0	8.5	4.20	10.5

SUMMARY

1. The condensation of 9-phenylxanthydrol with 1-phenyl-3-methylpyrazolone-5, which leads to the formation of 9-phenyl-9-(1'-phenyl-3'-methyl-4',5'-dihydro-5'-oxo-4'-pyrazolyl)-xanthene, may be carried out in both alcohol solution and acetic acid solution.

2. The products of the condensation of arylcarbinols with 1-phenyl-3-methylpyrazolone-5 in alkaline aqueous alcohol solutions are decomposed by diazo-compounds.

3. The dissociation of 1-phenyl-3-methyl-4-(9-phenyl-10-methyl-9,10-dihydroacridyl-9)-pyrazolone-5 in neutral solutions takes place slowly.

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* Original Russian pagination. See C.B. Translation.

THE SYNTHESIS OF 2-VINYLTHIOPHENE AND 2-VINYLDIBENZOTHIOPHENE

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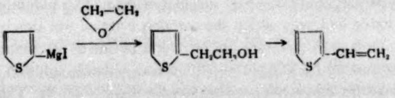
The study of vinyl derivatives of the thiophene series is undoubtedly of not only theoretical but also practical interest in view of the fact that there are indications that their polymers have valuable properties. At the same time the synthesis of these compounds has been insufficiently worked out, their properties have not been fully characterized and the data which are available are contradictory [1-3]. In addition, none of the workers who have studied these compounds have checked the purity of 2-vinylthiophene and 2-vinyldibenzothiophene, either from the elementary composition or from an analysis for vinyl groups.

2-Vinylthiophene was first prepared [4] in 1941, and later by Nazzaro and Bullock [3] in 1946, starting from methyl thienyl ketone, which was reduced to the carbinol and dehydrated over alumina. Strassburg and coworkers [5] suggested the low-temperature condensation of vinyl chloride and 2-thienyl magnesium bromide in the presence of cobalt chloride. Emerson and Patrick [6] carried out the chlorethylation of thiophene with paraldehyde and hydrogen chloride followed by removal of hydrogen chloride with pyridine. In 1948 Schick and Hartough [2] prepared 2-vinylthiophene from thienylethanol, synthesized by condensation of 2-thienyl sodium with ethylene oxide. All these methods gave yields of 30-40%, and only in isolated cases was a yield of 54% obtained.

We attempted to prepare 2-vinylthiophene by the most simple method, namely the condensation of thienyl magnesium iodide with acetaldehyde, taking into consideration the fact that the literature gives only very general indications [7] of the fundamental possibility of carrying out the synthesis. As a result of the ready dehydration of the secondary carbinol (which is brought about by traces of the iodine present), we encountered a number of difficulties, not only in the actual synthesis process, but also in the isolation process, since a whole variety of products was obtained: thiophene, iodothiophene, methylthienylcarbinol and vinylthiophene. This mixture was difficult to separate into pure products. The yield of pure 2-vinylthiophene amounted to approximately 15%. In later work we replaced the acetaldehyde by ethylene oxide. The primary alcohol obtained was dehydrated over powdered potassium hydroxide. The yield of 2-vinylthiophene amounted to 25%. The conditions for the preparation of 2-vinylthiophene corresponded to the conditions described in an article by Scully and Brown [8] which was published while our work was being carried out. After making certain changes in the reaction conditions we obtained 2-vinylthiophene in 50% yield.



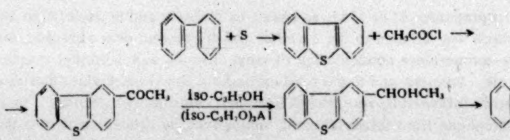
2-Vinyldibenzothiophene. Literature data on the synthesis are limited to a single work by R. Flowers and L. Flowers [9] and their two patents [10]. These authors prepared the monomer, and also a polymer, with a softening temperature of approximately 200° and dielectric properties as good as those of polystyrene.

The original dibenzothiophene was prepared by our modification of the method of Gilman and Jakoby [12]. The literature data on the synthesis of the intermediate product – acetyldibenzothiophene – are contradictory in relation to the preparation and yield of this product [11, 14]. In this process, as a rule, the diacetyl derivative is obtained with the monoacetyl compound. For the acetylation reaction we chose the best conditions for the preparation of the monoketone. In addition, we found that of the other solvents tried by us the most convenient was a benzene-toluene mixture, instead of the carbon disulfide or nitrobenzene usually recommended. The reaction in the benzene-toluene mixture takes place with less tar formation and with greater yield of the monoacetyl derivative. The products of acetylation of the solvent, formed in a side reaction, are readily removed by distillation. The yield of the monoacetyl derivative amounted to more than 55%, which was not attained when the reaction was carried out in carbon disulfide or in nitrobenzene.

The monoacetyl derivative obtained by us using these reaction conditions consisted, as other authors have also found [11-14], of a mixture of 2- and 3-acetyldibenzothiophenes in which, in our case, the 3-acetyldibenzothiophene predominated. The total yield of 2-acetyl-dibenzothiophene, however, was no less in the benzene-toluene mixture than when carbon disulfide or nitrobenzene were used as solvents. Moreover, the use of nitrobenzene yields a product contaminated with tarry substances which are difficult to remove by distillation and recrystallization of the product.

For the first time for this compound, we used the Meerwein-Ponndorf reaction for the reduction of the acetyl derivative to the carbinol. The reaction is convenient in that no high-pressure apparatus is required for carrying it out; it is simple and selective. The dehydration of the carbinol was carried out over alumina at 320° and a residual pressure of 5-10 mm mercury [9].

The overall scheme for the preparation is given below.



The aim of the present work included the improvement of the synthesis at all its stages and a study of the properties of the vinyl derivatives of thiophene and dibenzothiophene. Particular attention was paid to the preparation of these monomers in the purest state in order to study their physico-chemical constants and to carry out further work on polymerization kinetics.

The vinyl derivatives obtained were analyzed using the method of iodination with iodine chloride.

EXPERIMENTAL

The Synthesis of 2-vinylthiophene

The preparation of 2-iodothiophene was carried out by iodination of thiophene in the presence of mercuric oxide [15]. The yield of purified product with b.p. 80° (20 mm) amounted to 75%.

The preparation of thienylethanol. 70 g of ethylene oxide dissolved in anhydrous benzene was added rapidly through a dropping funnel with stirring and cooling to –10° to a flask fitted with reflux condenser and containing thienyl magnesium iodide prepared from 16 g magnesium and 130 g iodothiophene dissolved in absolute ether. When the ethylene oxide had been added the reaction mixture was slowly heated to room temperature and then heated on a water bath until the ether boiled over a period of 30 minutes. The reaction mixture was left overnight and then decomposed by an aqueous ammonium chloride solution with cooling by ice. Dilute hydrochloric acid was added after the decomposition process was complete. The contents of the flask were transferred to a separating funnel, the ether-benzene solution removed, and the aqueous solution extracted with ether. The combined ether extracts were washed, dried with anhydrous sodium sulfate, and the residue after removal of the solvent distilled in vacuo (from $1.6 \cdot 10^{-1}$ to $5.0 \cdot 10^{-1}$ mm mercury). The distillation yielded 6 fractions (see Table).

A second distillation of the 5th fraction gave pure thienylethanol with b.p. 74° (0.5 mm), n_D^{20} 1.5500, and a characteristic odor of roses.

Found %: S 24.76%. C_6H_8OS. Calculated %: S 25.00.

Fraction No.	Boiling point	n_D^{20}	Carbinol concentration (%)	Weight (in g)	Assumed composition of the mixture
1	42—43°	1.5762	20	25	Vinylthiophene, thiophene, iodothiophene
2	43—45	1.5720	50	15	Vinylthiophene, iodothiophene, thienylethanol
3	60—63	1.5652	70	10	Iodothiophene, thienylethanol
4	63—72	1.5562	84	20	Thienylethanol, iodothiophene
5	72—74	1.5510	100	20	Thienylethanol
6	78—90	—	—	10	Thienylethanol, polymers

In subsequent experiments the carbinol was not given further purification and fractions 3, 4 and 5 were dehydrated directly.

The preparation of 2-vinylthiophene. 50 g crude thienylethanol, copper turnings and powdered potassium hydroxide were placed in a Wurtz flask of 100 ml capacity. The flask was connected to a Liebig condenser and a receiver cooled by solid carbon dioxide. The pressure in the apparatus was reduced to 40-50 mm mercury and the reaction flask heated evenly using an open heater. As the reaction developed the degree of heating was reduced. The vinylthiophene which distilled over was collected, together with a small quantity of water, in the receiver. The product obtained was extracted with ether, the ether solution was washed with water, dried with anhydrous sodium sulfate and the solvent distilled off in vacuo. Vacuum distillation of the residue gave pure 2-vinylthiophene with a vinyl group content, according to analysis, of 100%:

0.1846 g material: 33.6 ml 0.1 N $Na_2S_2O_3$. % vinyl compound found: 100.

2-Vinylthiophene is a transparent, colorless volatile liquid with a sharp unpleasant odor. It has to be stored in sealed cooled ampoules.

B. p. 65.5-66.5° (48 mm), n_D^{20} 1.5722, d_4^{20} 1.0410, MR_D 34.83.

Found %: C 65.31; H 5.52. C_6H_6S. Calculated %: C 65.45; H 5.45.

Literature data: b.p. 63° (50 mm) [1]; 65.5-66.5° (48 mm) [2]; n_D^{23} 1.5612[3]; n_D^{25} 1.5698 [1]; n_D^{20} 1.5720 [2]; d_4^{20} 1.0429 [3].

The Synthesis of 2-vinyldibenzothiophene

Dibenzothiophene was prepared according to the method of Gilman and Jakoby [12]. The method for separating the synthesized product was slightly modified. Thus instead of the extraction with methyl alcohol using large quantities of the latter and the formation of supersaturated solutions, as recommended by the authors, but which is inconvenient in practice, we carried out a vacuum distillation. Before distillation the product was dried by washing with a small quantity of methyl alcohol. A second distillation gave a very pure product, boiling at 160° (4 mm) and forming beautiful long needles with m.p. 99° on recrystallization from methyl alcohol.

Found %: C 78.20; H 4.33. $C_{12}H_8S$. Calculated %: C 78.26; H 4.35.

The preparation of acetyldibenzothiophene. 60 g dibenzothiophene and 40 g acetyl chloride dissolved in a mixture of 250 ml benzene and 150 ml toluene were added to a three-necked flask of 1.5-2.0 liters capacity, fitted with stirrer, reflux condenser and tube for the addition of aluminum chloride. The mixture was cooled to 0° and 120 g of anhydrous aluminum chloride added gradually to it in small portions over a period of 2-3 hours. The reaction was continued with stirring for 3-4 days, the temperature of the reaction mixture being maintained between 0 and +10°. The reaction mixture was decomposed by 5% hydrochloric acid with vigorous stirring and cooling by ice. The benzene-toluene solution was washed thoroughly with sodium carbonate solution and water, then dried with anhydrous sodium sulfate. The solvent, together with a small quantity of acetophenone formed as a by-product, was distilled off and the residue solidified to a hard mass. The main bulk was distilled at 180-200° (2 mm) and proved to be a mixture of 2- and 3-acetyldibenzothiophenes. The yield of the mixture of isomers was more than 55%, of which the 2-acetyldibenzothiophene made up approximately 20%, calculated on the original dibenzothiophene. When the reaction was carried out in carbon disulfide or nitrobenzene as solvent the yield of the mixture of isomers amounted to 35-40%, of which the 2-acetyldibenzothiophene similarly amounted to approximately 20%.

When the distilled product was contaminated with tarry substances, as happened especially when working with nitrobenzene, purification was achieved by washing with cold ether, in which the product is almost insoluble. By boiling with ether it is likewise possible to separate 2-acetyldibenzothiophene, which is insoluble in boiling ether, from the mixture of 2- and 3-acetyldibenzothiophenes. 2-Acetyldibenzothiophene forms fine crystals with m.p. 111.5-112.5°.

Found %: C 74.46; H 4.58. $C_{14}H_{10}OS$. Calculated %: C 74.33; H 4.42.

The preparation of methyldibenzothienylcarbinol and its dehydration. Acetyldibenzothiophene, thoroughly purified by distillation and repeated recrystallization, was dissolved in anhydrous isopropyl alcohol and mixed with an exactly equivalent quantity of aluminum isopropoxide in such amount that the reaction mixture contained not more than 10-15% of the original ketone. The alcoholic solution of the reaction mixture was slowly heated under reflux for 2-3 hours. The mixture of acetone and isopropyl alcohol was then slowly distilled off over a period of 5-6 hours using an efficient column. At 82° the excess isopropyl alcohol was rapidly distilled off. The reaction product remaining in the flask was poured in small portions with stirring to a cooled dilute hydrochloric acid solution. When decomposition was complete the reaction mixture was extracted with benzene, the benzene solution washed with water and dried with sodium sulfate. The dry benzene solution was concentrated and used directly for the dehydration without isolation of the carbinol. An attempt to isolate the carbinol by vacuum distillation led to dehydration and polymerization in the distillation flask.

The dehydration reaction was carried out by us in a Pyrex glass column of 32-34 mm diameter and length 800 mm, heated by a tube-shaped furnace. The column was filled in the 250 mm long reaction zone with pieces of granulated alumina 7×5×5 mm and fitted with a thermocouple and automatic temperature regulator. The upper part of the column was fitted with a dropping funnel. The lower part of the column was fitted with a receiver cooled to low temperatures. A second trap connected to a manometer and vacuum pump was usually placed after the first receiver. When the apparatus had been assembled, the pump was switched on and the pressure reduced to 2-5 mm. The automatically regulated heater was then switched on. When the required temperature had been reached in the column, the benzene solution of the carbinol was introduced at a rate of 1-2 drops per second. It is convenient to keep the concentration of carbinol in the solution at 25-30%. A small quantity of phenyl-β-naphthylamine was added to the carbinol solution as an inhibitor. When the carbinol solution reached the reaction space, 50-100 ml of pure dry benzene was added dropwise, but at a somewhat faster rate than the working solution of the carbinol. Heating by the furnace was then stopped and at 30-60° the system was opened to the atmosphere. Air must not be allowed to reach the column during operation, since this leads to a lowering of the yield and contamination of the product. Before a subsequent experiment was carried out, the catalyst in the column was regenerated by the passage of a current of air at 500°. It should be borne in mind that rapid passage of air during regeneration may lead to strong local overheating and fusion of the material to the walls of the column.

The preparation of 2-vinyldibenzothiophene. The dehydration of the methyldibenzothienylcarbinol was carried out at 320 ± 20° and a residual pressure of 5-10 mm. The crude product was purified by recrystallization from methyl alcohol with cooling by solid carbon dioxide. Repeated crystallization gave needle-shaped crystals with m.p. 42°. From an analysis for vinyl groups the product contained 98.8% vinyldibenzothiophene.

0.1010 g material: 9.5 ml 0.1 N $Na_2S_2O_3$. % vinyl compound found: 98.8.

2-Vinyldibenzothiophene: b.p. 167° (0.5 mm), m.p. 42°.

Found %: C 80.30; H 5.00. $C_{14}H_{10}S$. Calculated %: C 80.00; H 4.82.

Literature data: m.p. 45° [9].

SUMMARY

1. A method has been worked out for the preparation of 2-vinylthiophene from thienyl magnesium iodide and ethylene oxide in 50% yield.

2. A method has been worked out for the preparation of acetyldibenzothiophene and its reduction to the carbinol by the Meerwein-Ponndorf reaction.

3. Hitherto unknown physico-chemical constants of the monomers have been evaluated and known constants redetermined.

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ESTERS OF ISOCYANATOPHOSPHORIC ACID AND THEIR DERIVATIVES

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A number of esters of urethanphosphoric acids of general formula (I) have recently been synthesized [1]. It is known [2] that when many urethans are heated alcohol is split off with the formation of isocyanates: – NHCOOR → – NCO. It might be expected that thermal decomposition of urethanphosphoric esters would lead to the formation of isocyanatophosphoric esters (II).

$$\underset{(I)}{(RO)_2PONHCOOR'} \xrightarrow{-R'OH} \underset{(II)}{(RO)_2PONCO}$$

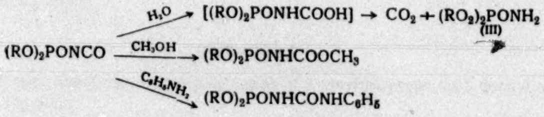
Indeed, when the esters (I) are vacuum distilled, substances are formed which differ sharply in physical and chemical properties from the original materials. A study of their chemical properties has shown that they are the hitherto unknown esters of isocyanatophosphoric acid of general formula (II).

The esters of methylurethanphosphoric acids (I, R = CH_3) were usually employed for the preparation of the esters (II). The esters of ethyl- and isopropylurethanphosphoric acids (I, R = C_2H_5, iso-C_3H_7) react in analogous fashion. Table 1 gives the yields, physical properties and analysis results for the esters (II).

TABLE 1

Specimen No	R	Boiling point (pressure in mm)	d_{20}^{20}	n^{20}	Yield (%)	Formula	Analysis results (%)		
							element	found	calcd.
1	CH_3 . . .	75—76° (4)	1.3136	1.4280	66	$C_3H_6O_4NP$	N	9.40, 9.35	9.27
2	C_6H_5 . . .	184—186 (5)	1.2828	1.5470	89	$C_{13}H_{10}O_4NP$	N	4.81, 4.74	5.09
3	p-BrC_6H_4 .	250 (10), m.p. 72—74	—	—	64	$C_{13}H_8O_4NBr_2P$	Br	36.84, 37.06	36.95

All the isocyanatophosphoric esters exhibit the characteristic reactions of the NCO-group. They react with water and atmospheric moisture to form esters of phosphamic acid (amidophosphoric acid). The esters of isocyanatophosphoric acid react with methyl alcohol to give quantitative yields of the original methylurethanphosphoric esters. An analogous reaction takes place with other alcohols. With aniline, esters of N-phenylcarbamido-N'-phosphoric acids are formed.



$$(RO)_2PONCO \xrightarrow{H_2O} [(RO)_2PONHCOOH] \rightarrow CO_2 + \underset{(III)}{(RO_2)_2PONH_2}$$

$$(RO)_2PONCO \xrightarrow{CH_3OH} (RO)_2PONHCOOCH_3$$

$$(RO)_2PONCO \xrightarrow{C_6H_5NH_2} (RO)_2PONHCONHC_6H_5$$

Dimethyl isocyanatophosphate is much more reactive than the diphenyl and di-p-bromophenyl esters. They are extraordinarily sensitive to atmospheric moisture and react with water with the production of great heat and vigorous evolution of carbon dioxide. The diphenyl ester is decomposed by water in approximately half an hour while the di-p-bromophenyl ester is decomposed in 2-3 hours. Unlike the diphenyl and di-p-bromophenyl esters, the dimethyl ester on treatment with water does not give the dimethyl ester of phosphamic acid (amidophosphoric acid) (III, R = CH_3) in a form which can be isolated chemically pure. The dimethyl ester also reacts much more vigorously with alcohols and aniline than do the other esters.

We have used the reaction of isocyanatophosphoric esters with alcohols for the synthesis of a number of new esters of urethanphosphoric acids which could not be prepared by the method described earlier [1]. The yields, melting points and analysis results for the esters of general formula $(RO)_2PONHCOOR'$ are given in Table 2.

TABLE 2

Substance №	R	R'	Yield (%)	Melting point	Formula	Analysis results: element	found	calcd.
1	CH_3	C_2H_5	98	Liquid	$C_5H_{12}O_5NP$	N	6.63, 6.60	7.10
2	CH_3	iso -C_3H_7	98	Liquid	$C_6H_{14}O_5NP$	N	6.17, 6.15	6.63
3	C_6H_5	n -C_4H_9	56*	Liquid	$C_{17}H_{20}O_5NP$	—	—	—
4	C_6H_5	iso -C_4H_9	51*	Liquid	$C_{17}H_{20}O_5NP$	—	—	—
5	C_6H_5	$CH_2C_6H_5$	78	79—81°	$C_{20}H_{18}O_5NP$	N	3.57, 3.72	4.60
6	$[(C_6H_5O)_2PONHCOO]_2$	CH_2CH_2	50	124—126 (decomp.)	$C_{27}H_{24}O_{10}N_2P_2$	N	4.79, 4.92	4.60
7	p-BrC_6H_4	n -C_4H_9	97	61—63	$C_{17}H_{18}O_5NPBr_2$	Br	31.98, 32.11	31.56
8	p-BrC_6H_4	$CH_2C_6H_5$	93	113—115	$C_{20}H_{16}O_5NPBr_2$	Br	29.47, 29.26	29.57

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* Isolated as the sodium salt.

Substances 1-4 were very viscous colorless liquids. On vacuum distillation they decomposed into their original components. Substances 3 and 4 could be isolated in the form of crystalline sodium salts. The low yield of the salts is due to the difficulty of purification. Substances 1 and 2 do not form crystalline salts. Substances 5-8 were colorless crystalline compounds, insoluble in water, soluble in alcohol, benzene, chloroform and acetone, insoluble in petroleum ether.

EXPERIMENTAL

Dimethyl isocyanatophosphate. 19.6 g dimethyl methylurethanphosphate was vacuum distilled from a Claisen flask fitted with a fractionating column. The first distillation yielded 15.6 g (80% of the product taken for the reaction) of liquid with b.p. 84-85° (7 mm) which proved to be a mixture of dimethyl isocyanatophosphate and the original ester. A second distillation yielded two fractions: 1st b.p. 75-76° (4 mm), 7.1 g; 2nd b.p. 80-100° (4 mm), 6.6 g. The liquid with b.p. 75-76° was pure dimethyl isocyanatophosphate. Distillation of the 2nd fraction yielded a further 3.5 g of pure ester. Thus after the 3rd fractionation 10.6 g (66%) of dimethyl isocyanatophosphate had been obtained.

Dimethyl N-phenylcarbamidophosphate. 3 g (0.02 mole) of dimethyl isocyanatophosphate was dissolved in 5 ml absolute ether. A solution of 1.9 g (0.02 mole) aniline in 5 ml ether was added with cooling by ice. The precipitate obtained was filtered off and washed with ether. Yield 3.4 g (70%). When recrystallized from water the product melted at 136-137° and gave no depression with known dimethyl N-phenylcarbamidophosphate [3].

Diphenyl isocyanatophosphate was obtained in 89% yield by a single vacuum distillation of diphenyl methylurethanphosphate.

Diphenyl phosphamate (amidophosphate). 2.75 g diphenyl isocyanatophosphate was treated with 10 ml water. After approximately 1/2 hour the liquid material had been converted into the crystalline phosphamate (amidophosphate). Yield 2.5 g (96%). The unpurified product melted at 143-146°; m. p. 148-150° after recrystallization from chloroform, which agrees with the literature data [4]. A mixture of the substance with known diphenyl phosphamate (amidophosphate) gave no depression.

Diphenyl N-phenylcarbamidophosphate. A solution of 0.68 g aniline in ether was added dropwise to an ethereal solution of 2.01 g diphenyl isocyanatophosphate. After several minutes the solution yielded a colorless fine crystalline precipitate. Yield 2.66 g (98%). Recrystallization from alcohol yielded colorless needle-shaped crystals with m.p. 155-156°.

Found %: N 7.58, 7.49. $C_{19}H_{17}O_4N_2P$. Calculated %: N 7.60.

Diphenyl carbamidophosphate was obtained by treating diphenyl isocyanatophosphate with aqueous ammonia. The compound is readily soluble in ammonia and alkali. M.p. 199-200° (from alcohol).

Found %: N 9.35, 9.36. $C_{13}H_{13}O_4N_2P$. Calculated %: N 9.58.

Di-p-bromophenyl isocyanatophosphate was prepared by a method analogous to that used for the preparation of the diphenyl ester.

Di-p-bromophenyl phosphamate (amidophosphate) was obtained in 85% yield by treatment of di-p-bromophenyl isocyanatophosphate with water. The reaction took place slowly over a period of 2-3 hours. When heated to 60-70° the reaction was complete in several minutes. The unpurified product had m.p. 177-181°; m.p. 186-188° after recrystallization from aqueous alcohol.

Found %: Br 39.56, 39.44. $C_{12}H_{10}O_3NBr_2P$. Calculated %: Br 39.31.

Di-p-bromophenyl N-phenylcarbamidophosphate. 0.2 g di-p-bromophenyl isocyanatophosphate was dissolved in 3 ml ether and a mixture of 0.5 g aniline and 0.5 ml ether added to the solution. The precipitate obtained was filtered off and recrystallized from acetonitrile. Yield 0.2 g (80%), colorless needles, m.p. 170-171° (with decomp.).

Found %: Br 29.97, 30.17. $C_{19}H_{15}O_4N_2Br_2P$. Calculated %: Br 30.42.

Dimethyl ethylurethanphosphate. 1.2 g anhydrous alcohol was poured gradually into 3.02 g dimethyl isocyanatophosphate. The reaction was accompanied by a considerable evolution of heat. The excess of alcohol was removed under vacuum at 50°. Yield 3.86 g.

Dimethyl isopropylurethanphosphate was prepared in analogous fashion.

Diphenyl n-butylurethanphosphate. 1.48 g anhydrous n-butyl alcohol was poured into 5.5 g diphenyl isocyanatophosphate. The reaction was accompanied by a slight evolution of heat. The viscous oil obtained was treated with a mixture of 10 ml 40% caustic soda solution and 5 ml methyl alcohol. The crystalline precipitate of the sodium salt of the ester was filtered off and dried. Weight 7.6 g (102%) (caustic soda impurity). The sodium salt of the ester was purified by extraction several times with boiling benzene and precipitation from benzene solution with petroleum ether. Yield of purified salt 4 g. M.p. 161-164° (with decomp.).

Found %: N 3.85, 3.70. $C_{17}H_{19}O_5NPNa$. Calculated %: N 3.77.

Diphenyl isobutylurethanphosphate. The reaction was carried out in a fashion analogous to the preceding reaction using the same quantities of starting materials. The thick oil obtained was treated with 15 ml 40% caustic soda solution. The precipitate of the salt of the ester was filtered off and dried. Weight 7.25 g (106%). The precipitate was dissolved in the minimum quantity of hot alcohol, the solution filtered and a 10-fold excess of benzene added. After a week a crystalline precipitate of the salt of the ester was obtained. Weight 3.6 g. M. p. 188-191° (with decomp.).

Found %: N 3.80, 3.60. $C_{17}H_{19}O_5NPNa$. Calculated %: N 3.77.

Diphenyl benzylurethanphosphate. 2.2 g of benzyl alcohol was added to 5.5 g diphenyl isocyanatophosphate. The viscous mass obtained was shaken up with 5% caustic soda solution until completely dissolved (5 portions of 20 ml). The alkaline extracts were combined, the solution filtered and acidified with dilute hydrochloric acid. An oil separated and rapidly crystallized. Yield 6 g. The product was purified by precipitation from benzene solution with petroleum ether.

The tetraphenyl ester of dicarbaminylethylene glycol N,N'-bis-phosphoric acid. 0.62 g glycol was added to 5.5 g diphenyl isocyanatophosphate. The mixture became hot and on cooling was converted into a viscous, and then into a glassy mass. The product was dissolved in 50 ml 5% caustic soda solution and precipitated with dilute hydrochloric acid. The viscous mass obtained was separated from the water by decantation, dissolved in benzene and precipitated with petroleum ether. Colorless amorphous powder. Yield 3 g.

Di-p-bromophenyl n-butylurethanphosphate. 0.37 g n-butyl alcohol was added to 2.2 g di-p-bromophenyl isocyanatophosphate. The reaction was accompanied by moderate evolution of heat. The product crystallized on cooling. The crystals were washed on the filter with water until the odor of butyl alcohol had disappeared, dried, and recrystallized from aqueous alcohol. Yield 2.5 g.

Di-p-bromophenyl benzylurethanphosphate was prepared by a method analogous to that of the last synthesis. Yield 2.5 g. The product was purified by precipitation from benzene solution with petroleum ether.

SUMMARY

1. It has been shown that the thermal decomposition of esters of urethanphosphoric acids lead to the formation of esters of isocyanatophosphoric acid.

2. Several new esters of urethanphosphoric acids have been prepared from the esters of isocyanatophosphoric acid.

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STUDIES ON THIOSULFONIC ACIDS

II. SOME ALKYL ESTERS OF PROPANE-2-THIOSULFONIC ACID AND 2-METHYLPROPANE-1-SULFONIC ACID

B. G. Boldyrev and T. A. Trofimova

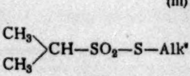
In previous works [1, 2] on the study of the antibacterial properties of alkyl esters (I) of alkanethiosulfonic acids with a straight chain of carbon atoms (from C_1 to C_4) we showed that these compounds possess a broad spectrum of antibacterial activity and in experiments in vitro exhibit an appreciable bacteriostatic (and corresponding fungistatic and protozocidic) action on gram-positive, gram-negative and acid-resistant bacteria, various fungi, protozoa, etc.; the greatest activity against all the forms of bacteria tested was exhibited, as a rule, by the isopropyl (II) and isobutyl (III) esters of alkanethiosulfonic acids. For this reason we thought it of interest to synthesize and study the antibacterial properties of alkyl esters of thiosulfonic acids containing these same radicals on the oxidized sulfur, i. e. the alkyl esters (IV) and (V) of propane-2-thiosulfonic and 2-methylpropane-1-thiosulfonic acids.

$$\text{Alk–SO}_2\text{–S–Alk'}$$

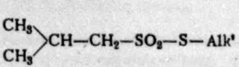
(I)

(II) $\text{Alk'} = \text{CH(CH}_3)_2$

(III) $\text{Alk'} = \text{CH}_2\text{CH(CH}_3)_2$



(IV)



(V)

With this aim and by well-known methods [3, 4] we prepared propane-2-sulfonyl chloride and 2-methylpropane-1-sulfonyl chloride, and by the reaction of the latter with an aqueous solution of potassium bisulfide synthesized the corresponding salts (VI) and (VII) of the thiosulfonic acids, which had not been prepared hitherto.

$$\text{Alk-SO}_2\text{Cl} + 2\text{KHS} \rightarrow \text{Alk-SO}_2\text{-SK} + \text{KCl} + \text{H}_2\text{S} \qquad (1)$$

(VI) $\text{Alk} = \text{CH(CH}_3)_2$

(VIII) $\text{Alk} = \text{CH}_2\text{CH(CH}_3)_2$

The colorless crystalline thiosulfonates (VI) and (VII) were separated from the reaction mass, recrystallized from anhydrous alcohol, and then used for the synthesis of the esters (IV) and (V).

$$\text{Alk-SO}_2\text{-SK} + \text{Alk'Br} \rightarrow \text{Alk-SO}_2\text{-S-Alk'} + \text{KBr} \qquad (2)$$

This reaction was carried out in aqueous acetone with prolonged heating on a water bath. After separation from the reaction mass and vacuum distillation 12 alkyl esters of propane-2-thiosulfonic and 2-methylpropane-1-thiosulfonic acids, which have not been previously described in the literature were prepared (Table 1). Like the alkyl esters of other alkanethiosulfonic acids [1, 2, 5], they are colorless oily liquids with a stable sharp odor of garlic or onion, sparingly soluble in water, miscible in all proportions with the usual organic solvents. The esters are quite stable, not only at room temperatures but also when heated to 120-140°, and are readily distilled in vacuo at a residual pressure of 1-2 mm without decomposition.

Microbiological examination of these compounds carried out by the USSR Academy of Sciences Institute of Microbiology[*] did not, however, confirm our expectations: in tests in vitro the alkyl esters of thiosulfonic acids with a branched chain of carbon atoms not only did not exceed in antibacterial activity the analogóus esters of thiosulfonic acids of normal structure, but often showed a lower activity, though only to a small extent (Table 2). Certainly, the alkyl esters of 2-methylpropane-1-thiosulfonic acid (V) are more active in their action on Staphylococcus aureus and certain fungi than the analogous esters of butane-1-thiosulfonic acid and many other esters described by us earlier [1, 2, 5]; nevertheless, even among the latter we found some esters with similar antibacterial properties.

TABLE 1

Alkyl Esters of Propane-2- thiosulfonic and 2-Methylpropane-1- thiosulfonic Acids of General Formula $Alk-SO_2-S-Alk'$

Specimen No.	Alk	Alk'	Boiling point (at 1-2 mm)	d_{20}^{20}	n_D^{20}	MR_D		Sulfur content (%)		Yield (%)
						found	calculated[*]	found	calculated	
1	$(CH_3)_2CH$	CH_3CH_2	100—101°	1.1597	1.5215	42.45	42.52	38.37	38.11	58.5
2		$CH_3CH_2CH_2$ . . .	108—109	1.1272	1.4954	47.09	47.14	35.38	35.18	54.0
3		$(CH_3)_2CH$	96—97	1.1193	1.4942	47.27	47.14	35.12	35.18	34.0
4		$CH_2=CH-CH_2$.	102—103	1.1580	1.5039	46.73	46.67	35.72	35.57	62.3
5		$CH_3CH_2CH_2CH_2$.	112—113	1.0888	1.4852	51.70	51.76	32.54	32.66	61.3
6		$(CH_3)_2CHCH_2$ . .	104—105	1.0978	1.4920	51.88	51.76	32.82	32.66	33.6
7	$(CH_3)_2CHCH_2$	CH_3CH_2	108—109	1.1183	1.4906	47.18	47.14	35.10	35.18	70.0
8		$CH_3CH_2CH_2$ . . .	115—116	1.0884	1.4879	51.95	51.76	32.55, 32.49	32.66	62.5
9		$(CH_3)_2CH$	104—105	1.0964	1.4886	51.64	51.76	32.51, 32.57	32.66	39.1
10		$CH_2=CH-CH_2$.	110—111	1.1187	1.5039	51.42	51.29	32.73	33.00	72.3
11		$CH_3CH_2CH_2CH_2$.	123—124	1.0599	1.4821	56.59	56.37	30.36	30.49	54.6
12		$(CH_3)_2CHCH_2$ . .	118—120	1.0669	1.4858	56.59	56.37	30.47	30.49	36.2

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[*] As in previous works [1, 2, 5] the refractivities of the $>SO_2$ group and of sulfide sulfur $-S-$ are taken as 8.63 and 8.00 respectively (mean values); the exaltation of the $-SO_2-S$ group is taken as +0.6.

Thus when the structure of the esters (I) of alkanethiosulfonic acids is altered within narrow limits their activity relative to different bacteria depends mainly on the structure of the radical attached to the sulfide sulfur, but not on that on the oxidized sulfur.

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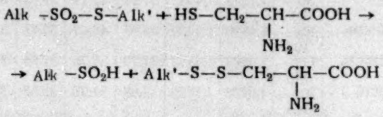
[*] We take this opportunity to express our gratitude to V. G. Drobotko, B. E. Eisenman and S. I. Zelepukha for carrying out the examination of our specimens.

TABLE 2

Antibacterial Activity of Alkyl Esters of Propane-1-thiosulfonic and Propane-2-thiosulfonic Acids in Vitro*

Specimen No.	Activity in dilutions							
	Bacteria types			Fungi types				
	Staphylococcus aureus	*B. Coli*	*Mycobacterium* B_5	*Penicillium*	*Aspergillus*	*Fusarium*	*Rhizopus*	*Mucor*
1	1:25000	1:25000	1:25000	1:25000	1:50000	1:50000	1:10000	1:10000
2	1:25000	1:25000	1:25000	1:50000	1:50000	1:50000	1:10000	1:10000
3	1:250000	1:100000	1:250000	1:100000	1:25000	1:250000	1:25000	1:25000
4	1:25000	1:25000	1:25000	1:50000	1:50000	1:50000	1:10000	1:10000
5	1:10000	1:5000	1:10000	—	—	—	—	—
6	1:250000	1:25000	1:100000	1:100000	1:10000	1:100000	1:5000	1:5000
7	1:50000	1:20000	1:20000	1:25000	1:50000	1:50000	1:10000	<1:10000
8	1:10000	1:20000	1:20000	1:25000	1:50000	1:50000	<1:10000	<1:10000
9	1:10000	1:25000	1:25000	1:250000	1:25000	1:250000	1:25000	—
10	1:20000	1:20000	1:20000	1:50000	1:50000	1:50000	<1:10000	<1:10000
11	1:20000	1:10000	1:10000	1:25000	1:50000	1:50000	<1:10000	<1:10000
12	1:10000	1:25000	1:25000	1:250000	1:100000	1:250000	1:25000	—

The antibacterial activity of these compounds is explained by some authors [6] as due to their ability to react with mercapto compounds, including cysteine and glutathione, which are important metabolites for the growth of bacteria. They suggest that as a result of a reaction of type (3), "blocking" of the sulfhydryl group of the metabolite takes place, and this causes a breakdown of the exchange processes of the bacterial cell.



$$\text{Alk}-SO_2-S-\text{Alk}'+HS-CH_2-\underset{\displaystyle NH_2}{\underset{|}{CH}}-COOH \rightarrow$$

$$\rightarrow \text{Alk}-SO_2H+\text{Alk}'-S-S-CH_2-\underset{\displaystyle NH_2}{\underset{|}{CH}}-COOH$$

The mechanism indicated for the action of thiosulfonic esters is not, of course, the only one possible, the more so since certain dialkyl disulfides, as we have found in our studies, exhibit a broad spectrum of antibacterial action equal to that of the esters (I), although their activity is considerably lower (Table 3).

However, it is only the combination of oxidized and sulfide sulfur characteristic of esters of thiosulfinic and thiosulfonic acids ($-SO-S-$ or $-SO_2-S-$) which is responsible for the high antibacterial activity of these compounds; dialkyl sulfoxides and dialkyl sulfones under the same conditions show no action (Table 3).

In accordance with the views put forward above on the mechanism of action of the thiosulfonic esters it should be expected that with a lowering of the stability of the $-S-S-$ bond in the esters (I) their tendency to split under the influence of mercapto compounds would be increased, while there should be a parallel increase in their antibacterial activity. At the same time, a change in the structure of the alkyl radicals in the alkyl esters (I) of alkanethiosulfonic acids cannot cause a sudden change in the strength of the $-S-S-$ bond and evidently cannot have a marked effect on the antibacterial activity of these compounds, which we have actually observed in the case of many of the substances in this group.

The increased activity of the isopropyl (II) and isobutyl (III) esters of alkanethiosulfonic acids enables us to suggest that their action is due to another cause: the radicals bound to the sulfide sulfur possibly play the role of a "guide" for the ester towards its place of action and facilitate penetration of the substance to the very plasma of the microorganism.

TABLE 3

Antibacterial Activity of Dialkyl Sulfides, Sulfoxides, Sulfones and Disulfides in Vitro•

Formula of substance	Activity in dilutions							
	Bacteria types			Fungi types				
	Staphylococcus aureus	*B. Coli*	*Mycobacterium* B_5	*Penicillium*	*Aspergillus*	*Fusarium*	*Rhizopus*	*Mucor*
$CH_3-CH_2-CH_2-S-CH_2-CH_2-CH_3$	0	0	0	0	0	0	0	0
$CH_3-CH_2-CH_2-SO-CH_2-CH_2-CH_3$	0	0	0	0	0	0	0	0
$CH_3-CH_2-CH_2-SO_2-CH_2-CH_2-CH_3$	0	0	0	0	0	0	0	0
$CH_3-CH_2-CH_2-CH_2-S-CH_2-CH_2-CH_2-CH_3$	1: 5000	0	0	0	0	0	0	0
$CH_3-CH_2-CH_2-CH_2-SO-CH_2-CH_2-CH_2-CH_3$	0	0	0	0	0	0	0	0
$CH_3-CH_2-CH_2-CH_2-SO_2-CH_2-CH_2-CH_2-CH_3$	0	0	0	0	0	0	0	0
$CH_3-CH_2-CH_2-S-S-CH_2-CH_2-CH_3$	1 : 5000	1 : 5000	1 : 25000	1 : 25000	1 : 5000	1 : 5000	1 : 5000	0

• Tables 2 and 3 show the minimum concentrations preventing the growth of the bacteria and fungi; zero indicates that no action on the cultures was detected at a dilution of the specimen of 1 : 5000, a minus indicates that tests were not carried out.

Lo Chien-Pen, Wilson and Croxall [7], introducing as a radical of this type the trichloromethyl group into the molecules of thiosulfonic esters, recently prepared the esters $R-SO_2-S-CCl_3$, evidently hoping to give them insecticidal properties; unfortunately the authors do not indicate in their work the physiological and antibacterial activity of these compounds.

At the same time it is to be expected that the trichloromethyl esters $R-SO_2-S-CCl_3$ should exhibit antibacterial properties, since the related alkyl esters $p-X-C_6H_4-SO_2-S-Alk$, prepared by us earlier [8] are often distinguished by a fairly marked antibacterial activity.

EXPERIMENTAL•

The thiosulfonic esters were prepared according to the well-known method described in detail by us earlier [9]; the intermediate products necessary for their synthesis – alkanesulfonates, sulfonyl chlorides and thiosulfonates – were also prepared by the usual methods [3, 4, 6]. The boiling points of the sulfonyl chlorides agreed with the literature data [10, 11].

The potassium salts of propane-2-thiosulfonic and 2-methylpropane-1-thiosulfonic acids were prepared by the reaction of the sulfonyl chlorides with an aqueous solution of potassium disulfide, with subsequent evaporation of the reaction mass to dryness and extraction of the thiosulfonates with butyl alcohol. After recrystallization from anhydrous alcohol they were obtained in the form of colorless crystalline substances, readily soluble in water and boiling alcohols, insoluble in benzene, chloroform, ether and acetone, with m.p. 242-243° and 235-236° respectively (with decomp.). In this process, 40.5 g propane-2-sulfonyl chloride and 31.4 g caustic potash, dissolved in 63 ml water and saturated with hydrogen sulfide, yielded 30.0 g of potassium propane-2-thiosulfonate, which amounted to 60.0% of the theoretical yield. The product crystallizes from butyl alcohol in the form of dense rhombic crystals and from ethyl alcohol in the form of thin six-sided plates.

Found %: S 35.84. $C_3H_7O_2S_2K$. Calculated %: S 35.96.

Similarly, 45.0 g 2-methylpropane-1-sulfonyl chloride and 32.5 g caustic potash, dissolved in 65 ml water and saturated with hydrogen sulfide,

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• Students A. T. Zakharchuk and L. G. Voskres took part in this work.

yielded 35.0 g of potassium 2-methylpropane-1-thiosulfonate (62.0%). The substance crystallizes from butyl alcohol in the form of very thin rhombic plates, and from ethyl alcohol in the form of thin square plates. This salt is slightly hygroscopic and resembles that described above in its solubility in various solvents.

Found %: S 33.42, 33.29. $C_4H_9O_2S_2K$. Calculated %: S 33.35.

The alkyl esters of the thiosulfonic acids were prepared by heating aqueous acetone solutions of the potassium thiosulfonates and alkyl bromides on a water bath for 10-20 hours in the case of the esters of normal structure and 70-120 hours for the isobutyl and isopropyl esters respectively. Ater distillation of the acetone, extraction and vacuum distillation, the esters were obtained in the form of colorless oily mobile liquids with a garlic-onion odor. They are very sparingly soluble in water, miscible in all proportions with the usual organic solvents, stable on heating to 120-140°, and are distilled in vacuo at a residual pressure of 1-2 mm. The yields and analyses of the esters are given in Table 1.

As an example we give a description of the synthesis of isopropyl 2-methylpropane-1-thiosulfonate. 30.0 g of potassium 2-methylpropane-1-thiosulfonate was dissolved in a mixture of 100 ml of acetone, freshly distilled over $KMnO_4$, and 17 ml water. 19.2 g of isopropyl bromide was added to the solution, after which the reaction mass was heated under reflux on the water bath for 120 hours. The solution was cooled, the precipitate of potassium bromide obtained was filtered off, the acetone distilled off on the water bath, the oily layer of the isopropyl ester removed in a separating funnel and the aqueous layer extracted with ether. The ether extracts were combined with the main product, washed with distilled water and dried with anhydrous sodium sulfate. After filtration and distillation of the ether the residue was vacuum distilled at a residual pressure of 1-2 mm. The yield of colorless product with b.p. 104-105° amounted to 11.9 g (39.1%).

SUMMARY

1. The potassium salts of propane-2-thiosulfonic acid and 2-methylpropane-1-thiosulfonic acid, which have not been described before, have been prepared and isolated by the reaction of the sulfonyl chlorides with an aqueous solution of potassium sulfide.

2. 12 alkyl esters of these thiosulfonic acids, which have not been described in the literature, have been synthesized.

3. The antibacterial activity of the esters prepared has been studied and suggestions have been put forward on the relation between their structure and their antibacterial action.

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** Russian translation.

REACTION OF DIALKYL ESTERS OF PHOSPHOROUS ACIDS WITH ALDEHYDES AND KETONES

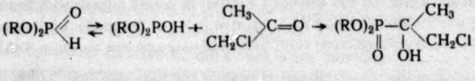
XIII. ESTERS OF α-HYDROXY-β-CHLOROISOPROPYLPHOSPHONIC AND 1,2-EPOXY-2-PROPYLPHOSPHONIC ACIDS

V. S. Abramov and A. S. Kapustina

The dialkyl esters of phosphorous acids react with some aldehydes and ketones in the absence of a catalyst. With some carbonyl compounds, for example with chloral [1], the reaction proceeds very rapidly and with much heat evolution, while with others, for example with nitrobenzaldehydes [2], it proceeds slowly and requires heating. The substituents present in these carbonyl compounds—chlorine in the first and the nitro group in the second case, evidently exert an influence on both the polarity and the reactivity of the carbonyl group. It was logical to assume that other carbonyl compounds with substituents will also react with the dialkyl esters of phosphorous acids in the absence of a catalyst. Consequently, we began to study the reaction of the dialkyl esters of phosphorous acids with halo-substituted ketones. Depending on the number of chlorine atoms in the molecule, the chloro-substituted acetones react differently with the dialkyl esters of phosphorous acids.

Monochloroacetone, the subject of study in the present communication, condenses with dialkylphosphorous acids with heating in the absence of a catalyst. The most favorable temperature for running the reaction is in the range 100-120°, and tarring occurs if a higher temperature is used. The reaction proceeds quite slowly and needs some time for its completion. Periodic measurement of the index of refraction was used to determine progress of the reaction.

Evidently, carbonyl compounds condense with the enol form of the dialkylphosphorous acids. The equilibrium of the latter, as has been shown in a number of studies [3], is shifted toward the keto form. When the reaction proceeds rapidly with the evolution of heat, then it must be assumed that it proceeds in the ionic form involving the $(RO)_2\bar{P}O$ ion; if the reaction proceeds without the evolution of heat and requires a longer time, then it probably proceeds in the molecular form. We are of the opinion that the condensation of chloroacetone with dialkylphosphorous acids proceeds in the molecular form and can be represented by the scheme



$$(RO)_2P\begin{matrix}\nearrow O\\ \searrow H\end{matrix} \rightleftarrows (RO)_2POH + \begin{matrix}CH_3\\ CH_2Cl\end{matrix}\!\!>C{=}O \rightarrow (RO)_2\underset{\underset{O}{\|}}{P}-\underset{\underset{OH}{|}}{C}\!\!<\!\begin{matrix}CH_3\\ CH_2Cl\end{matrix}$$

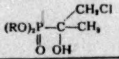
The obtained condensation products are listed in Table 1.

α-Hydroxy-β-chloroisopropylphosphonic acid and its phenyl ester was obtained by Conant and coworkers [4] by the respective treatment of the reaction products of phosphorous trichloride with chloroacetone with either water or phenol.

A study of the properties of the obtained esters is also of interest, in particular, their behavior toward alcoholic potassium hydroxide solution. We expected the cleavage of hydrogen chloride and the transformation of the condensation products into the esters of 1,2-epoxy-2-propylphosphonic acid. As was to be expected, the loss of hydrogen from the hydroxyl group and the formation of the oxide ring make the P-C bond stable. The obtained esters, shown in Table 2, distill without noticeable decomposition.

TABLE 1

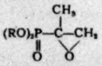
Esters of α-Hydroxy-β-chloroisopropylphosphonic Acid



R	Melting point	Yield (in %)	Amount of chlorine (in %)		Amount of phosphorus (in %)	
			found	calcd.	found	calcd.
CH_3	73—74°	58.7	17.15, 17.33	17.53	15.11, 15.02	15.30
C_2H_5	47—48	65.3	15.21, 15.11	15.41	13.50, 13.23	13.45
iso-C_3H_7	79—80	57.9	12.95, 12.97	13.73	12.05, 11.70	11.99
C_4H_9	Liquid	50.6	12.21, 12.25	12.39	10.70, 10.67	10.82
iso-C_4H_9	76—77°	48.4	12.24, 12.32	12.39	10.80, 10.92	10.82

TABLE 2

Esters of 1,2-Epoxy-2-propylphosphonic Acid



R	Boiling point (pressure in mm)	Yield (in %)	n_D^{20}	d_4^{20}	MR_D		Amount of phosphorus (%)	
					found	calc.	found	calc.
C_2H_5 . . .	96— 97°(6)	79.5	1.4305	1.1138	45.04	45.54	15.75, 15.80	15.98
iso-C_3H_7 .	95— 97 (6)	41.2	1.4252	1.0383	54.64	54.76	13.80, 13.90	13.96
C_4H_9 . . .	139—140 (5)	32.1•	1.4365	1.0313	63.46	64.00	12.25, 12.40	12.40
iso-C_4H_9 .	125—127 (6)	58.5	1.4333	1.0239	63.56	64.00	12.30, 12.30	12.40

• The cleavage reaction was run with the crude condensation product, and the yield is based on this. If the losses incurred in purifying the condensation product are taken into account, then the yield is roughly doubled.

EXPERIMENTAL

Preparation of Esters of α-Hydroxy-β-chloroisopropylphosphonic Acid. The condensation of the dialkylphosphorous acids with chloroacetone was run without a catalyst in sealed ampuls with heating on either a water or glycerin bath. Heating was terminated when the refractive index of the product failed to change. The conditions for the condensation of dialkylphosphorous acids with chloroacetone are shown in Table 3.

Usually the condensation products crystallized on cooling and were recrystallized from cyclohexane. The condensation product of dibutylphosphorous acid with chloroacetone remained liquid. The condensation product was purified by washing [5] it with sodium chloride solution, in which both the chloroacetone and dibutylphosphorous acid were soluble. The product was dried in a vacuum-desiccator to constant weight.

n_D^{20} 1.4500, d_4^{20} 1.0914, MR 70.54; Calc. 70.26.

The ethyl ester of α-hydroxy-β-chloroisopropylphosphonic acid, as long as it remained liquid, was purified in the same manner and had the following constants.

n_D^{20} 1.4520, d_4^{20} 1.2079, MR 51.71.

TABLE 3

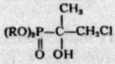
Value of R in dialkylphosphorus acids $(RO)_2POH$	Amount of reacted substances (in g)		Heating temperature	Time of heating (in hours)
	acid	chloroacetone		
CH_3	58.0	48.5	110—130°	20
C_2H_5	186.0	124.5	110—120	40
iso-C_3H_7.	49.8	27.8	100	120
C_4H_9	92.0	46.5	140—150	38
iso-C_4H_9	92.0	46.5	140—150	38

In another experiment the ester was distilled. The distillation proceeded with but slight decomposition. B. p. 139-140° (4 mm), n_D^{20} 1.4500, d_4^{20} 1.1978, MR 51.72; calc. 51.78.

The used methods of purification proved to be of equal value; after purification the ester soon crystallized.

Preparation of Esters of 1,2-Epoxy-2-propylphosphonic Acid. The esters were prepared in a flask, fitted with reflux condenser, stirrer and dropping funnel. Usually the starting ester was soluble in the alcohol and was added to an alcohol solution of potassium hydroxide. The reaction was first run with cooling, and was completed by heating to alcohol boil. The precipitate of potassium chloride was filtered. The alcohol was distilled off, and the product was vacuum-distilled. A pure substance was obtained after two-three consecutive distillations. The experiments on the cleavage of hydrogen chloride are summarized in Table 4, while the obtained esters of 1,2-epoxy-2-propylphosphonic acid are listed in Table 2.

TABLE 4

R in the esters  $(RO)_2P(=O)-C(CH_3)(OH)-CH_2Cl$	Amount of reactants				Amount of KCl precipitate (in %)
	starting ester (in g)	KOH (in g)	alcohol for dissolving the ester (ml)	alcohol for dissolving the KOH(ml)	
CH_3.	25.0	7.0	50	100	53.2
C_2H_5	161.0	44.0	100	250	86.3
iso-C_3H_7	20.0	3.9	25	80	91.6
C_4H_9	100 (crude product)	15.0	—	150	82.5
iso-C_4H_9	47.0	9.0	100	100	78.6

It proved impossible to isolate the methyl ester of 1,2-epoxy-2-propylphosphonic acid from the reaction product. In one experiment, where the cleavage of hydrogen chloride was run in absolute ethyl alcohol, the reaction product decomposed on distillation, and a hard, water-insoluble mass remained in the flask. In another experiment the cleavage of hydrogen chloride was run in methyl alcohol in the presence of calcium oxide for the purpose of combining with the liberated water. A gel-like product remained after distilling off the solvent.

SUMMARY

1. Dialkylphosphorous acids react with chloroacetone when heated in the absence of a catalyst to yield esters of α-hydroxy-β-chloroisopropylphosphonic acid.

2. Some new esters of 1,2-epoxy-2-propylphosphonic acid were obtained by the cleavage of hydrogen chloride from the obtained compounds.

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CYANINE DYES

VII. CYCLIZATION OF SECONDARY AROMATIC AMINES WITH VINYL ETHERS INTO ARYLQUINALDINIUM DERIVATIVES

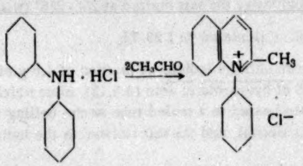
G. T. Pilyugin and E. P. Opanasenko

We had shown that the condensation of secondary aromatic amines with paraldehyde in acid medium results in ortho-cyclization of the pyridine ring with the formation of quaternary salts that are derivatives of quinaldine with aryl radicals on the nitrogen heteroatom [1]. These quaternary salts are capable of showing diverse chemical transformations at the methyl group in the α-position, found in conjugation with the electrophilic nitrogen [2]. Trimethinecyanine, monomethinecyanine and styryl derivatives were among the salts that were synthesized in this manner. Knowing that acetaldehyde, formed in the depolymerization of paraldehyde, plays an important role in the indicated reaction of secondary amines with paraldehyde, it seemed of interest to examine the condensation of secondary amines with other compounds that form acetaldehyde by a different type of chemical transformation (isomerization, hydrolytic transformations, etc.). Based on their chemical structure and properties the vinyl ethers can be such compounds, for on hydrolysis they form acetaldehyde, as had been shown even by A. M. Butlerov, A. Volkova and A. P. Eltekov [3-5]. As the result of the studies of A. E. Favorsky and M. F. Shostakovsky [6] the vinyl ethers have become readily available compounds in recent years, have assumed industrial importance, and are widely used in scientific research. Thus, a number of papers have been published, devoted to a study of the reactions of vinyl ethers and esters with primary aromatic amines [7].

In this communication we discuss the condensation of vinyl ethers with diphenylamine, phenyl-β-naphthylamine, o-tolyl-β-naphthylamine, p-methoxyphenyl-β-naphthylamine and p-tolyl-α-naphthylamine, as a result of which the quaternary N-arylquinaldinium salts were isolated.

The formation of the salts proceeded in accord with the scheme:

$$CH_2{=}CH{-}O{-}C_4H_9 + H_2O \xrightarrow{HCl} CH_2{=}CHOH \rightarrow CH_3CHO + C_4H_9OH$$



The isolated quaternary salts proved to be identical with the salts that we had synthesized from secondary aromatic amines and paraldehyde [1], which was confirmed by the complete analogy in properties, analytical data and the simpler chemical transformations. The condensation was run in sealed tubes (ampuls), flasks fitted with a stirrer, and in the presence of both concentrated and dilute (1 : 2) hydrochloric acid; as a reaction medium we used ethyl and butyl alcohols, xylene, aqueous alcohol and water. The experiments revealed that the quaternary salts are obtained in the same yield in water medium, but are more pure before purification. When the reaction was run in benzene, xylene and alcohol the reaction mass had to be treated with ether, since without this the salts crystallize with difficulty. The use of dilute hydrochloric acid increases the yield. It is preferable to prepare the salts in flasks, since this permits operating with larger quantities than when ampuls are used.

EXPERIMENTAL

The amines were condensed with vinyl ethyl and vinyl butyl ethers, but because of identical results only the experiments with vinyl butyl ether are given.

N-Phenylquinaldinium Perchlorate. A solution of 15 g of diphenylamine in 30 ml of xylene was prepared in a round-bottomed flask with stirring. The addition of 10 ml of hydrochloric acid (d 1.19) gave the diphenylamine salt as a precipitate. Then 30 ml of vinyl n-butyl ether (b.p. 93.7°) was gradually added from a dropping funnel with stirring, which resulted in much evolution of heat and conversion of the crystalline mixture into a homogeneous light-brown liquid. After self-heating had ceased the condensation was completed by heating at the boil for 2 hours, and then 500-700 ml of boiling water was added to dissolve the salt. The N-phenylquinaldinium perchlorate was isolated from the water layer by the addition of saturated potassium perchlorate solution. Pale yellow needle crystals deposited on cooling, which after recrystallization from water melted at 158-159°. The yield of the quaternary salt was 8.5 g (30%). The mixed melting point was not depressed.

Found %: Cl 11.32. $C_{16}H_{11}O_4NCl$. Calculated %: Cl 11.50.

N-Phenyl-5,6-benzoquinaldinium Iodide. A mixture of 2 g of phenyl-β-naphthylamine, 5 ml of benzene, 3 ml of hydrochloric acid (1 : 1) and 5 ml of vinyl butyl ether was sealed in an ampul and heated on the boiling water bath for 4 hours. The reaction mass was treated with 20 ml of saturated potassium iodide solution, heated to the boil, and filtered. Needle crystals of the salt deposited from the filtrate. After 2 recrystallizations from water the salt melted at 196-198°. The yield of the salt was 1.30 g (34%). The condensation of the salt with orthoformic ester gave carbocyanine with a maximum absorption at 644 mμ.

Found %: I 31.86; N 3.73. $C_{20}H_{16}NI$. Calculated %: I 31.97; N 3.52.

N-(o-Tolyl)-5,6-benzoquinaldinium Iodide. A mixture of 4.8 g of o-tolyl-β-naphthylamine, 3 ml of dilute hydrochloric acid (1:2) and 5 ml of vinyl butyl ether was sealed in a glass tube and heated on the water bath for 6 hours. The reaction product was treated several times with ether and dissolved in alcohol. The salt was precipitated from the hot alcohol solution by treatment with 25 ml of saturated potassium iodide solution, diluted with two volumes of water. After recrystallization from water the quaternary salt melted at 208-210°. The yield of the salt was 2.70 g (33.7%).

Found %: I 31.16; N 3.40. $C_{21}H_{18}NI$. Calculated %: I 30.86; N 3.40.

N-(p-Methoxyphenyl)-5,6-benzoquinaldinium Iodide. A mixture of 2.4 g of p-methoxyphenyl-β-naphthylamine, 2.5 ml of vinyl butyl ether, 4.5 ml of dilute hydrochloric acid (1:2) and 4 ml of benzene was heated in a sealed tube on the boiling water bath for 4 hours. The brown reaction mass was treated with ether, dissolved in alcohol, and the salt converted into the iodide by the addition of saturated potassium iodide solution with heating. After recrystallization from water the salt melted at 255-256° (with decompn.). Yield 1.2 g (26%).

Found %: I 29.51. $C_{21}H_{18}ONI$. Calculated %: I 29.72.

N-(α-Naphthyl)-6-methylquinaldinium Iodide. A solution of 1.5 g of p-tolyl-α-naphthylamine in 2 ml of benzene was treated with 1.2 ml of hydrochloric acid (d 1.19), after which 2 ml of vinyl butyl ether was added with cooling. This mixture was then heated in a sealed tube on the boiling water bath for 4 hours, after which it was treated with ether, dissolved in alcohol, and the salt isolated as the iodide. One gram (35%) of the salt was obtained after recrystallization.

Found %: I 30.73; N 3.78. $C_{21}H_{20}NI$. Calculated %: I 30.86; N 3.40.

SUMMARY

1. It was shown that the reaction of secondary aromatic amines with vinyl butyl and vinyl ethyl ethers in acid medium leads to ortho-cyclization of the pyridine ring with the formation of N-arylquinaldinium derivatives.

2. The following quaternary salts were isolated and characterized: N-phenylquinaldinium perchlorate, N-phenyl-5,6-benzoquinaldinium iodide, N-(o-tolyl)-5,6-benzoquinaldinium iodide, N-(p-methoxyphenyl)-5,6-benzoquinaldinium iodide and N-(α-naphthyl)-6-methylquinaldinium iodide. These salts are identical with the salts that we had synthesized earlier from the corresponding amines and paraldehyde.

3. It was shown that the quaternary arylquinaldinium salts are obtained in better yields by this method than by the paraldehyde method.

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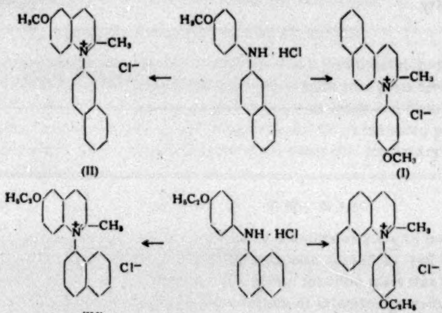
CYANINE DYES

VIII. SYNTHESIS OF ALKOXY DERIVATIVES OF QUATERNARY BENZOQUINALDINIUM SALTS AND THEIR TRANSFORMATIONS

G. T. Pilyugin, E. P. Opanasenko and N. A. Tsvetkova

We had shown that the reaction of secondary aromatic amines with paraldehyde leads to cyclization of the pyridine ring with the formation of quaternary quinaldinium salts with aryl radicals on the nitrogen heteroatom [1, 2].

As a continuation of these studies, we ran the cyclization of p-methoxyphenyl-β-naphthylamine and p-ethoxyphenyl-α-naphthylamine. It seemed of interest to obtain salts with alkoxy groups and to run a number of chemical transformations with them. The formation of the salts could proceed in accord with the schemes:



From the papers published by us it is known that the cyclization of phenyl-β-naphthylamine occurs at the naphthalene ring due to the greater mobility of the hydrogen atom in the α-position. The cyclization of phenyl-α-naphthylamine occurred at the phenyl radical [3]. A study of the isolated compounds revealed that under our conditions the cyclization of p-methoxyphenyl-β-naphthylamine occurred at the naphthalene ring. Here the methoxy group was without influence on the cyclization when compared with the unsubstituted amine. In the case of ethoxyphenyl-α-naphthylamine the cyclization was not at the benzene ring, as is the case with the unsubstituted amine, but instead it was at the naphthalene ring, which indicates the hindering effect exerted by the ethoxy group. The quaternary N-p-methoxyphenyl-5,6-benzoquinaldinium (I) and N-p-ethoxyphenyl-7,8-benzoquinaldinium (III) salts were isolated as the result of the reactions run by us. Other isomeric reaction products were not found. The obtained salts are homogeneous substances, and the dyes synthesized from them have a uniform absorption maximum. Symmetrical carbocyanines [4, 5] were synthesized from the obtained salts. The reaction of the salts with 2-β-acetanilinovinylbenzothiazole ethiodide and 2-β-acetanilinovinyldimethylindolenine methiodide gave symmetrical carbocyanines [6]. Condensation of the salts with quinoline ethiodide and p-dimethylaminobenzaldehyde gave the corresponding isocyanine and styryl derivatives [7-11].

EXPERIMENTAL

N-(p-Methoxyphenyl)-5,6-benzoquinaldinium Iodide. Into a glass ampul was charged 2.4 g of p-methoxyphenyl-β-naphthylamine, 10 ml of benzene and 1 ml of hydrochloric acid (d 1.19). After cooling the mixture was treated with 0.84 g of paraldehyde, the ampul sealed, and then heated on the boiling water bath for 3 hours. The reaction product was repeatedly washed with ether, dissolved in 10-15 ml of alcohol, converted into the iodide by the addition of 10 ml of saturated potassium iodide solution, heated to the boil, and filtered. The filtrate deposited golden-yellow crystals of the quaternary salt, m.p. 250-251°. The yield of the salt was 1.2 g (26%).

Found %: I 29.77, 29.86. $C_{21}H_{18}ONI$. Calculated %: I 29.72.

Bis-(1-p-methoxyphenyl)-5,6-benzoquinoline-2-(trimethinecyanine) Iodide. A mixture of 0.4 g of p-methoxyphenylbenzoquinaldinium iodide, 0.28 g of ethyl orthoformate, 3 ml of pyridine and 1 ml of acetic anhydride was heated at the boil for 40 minutes. In about 20 minutes lustrous green crystals began to deposit from the boiling reaction mass, which after cooling were filtered and recrystallized from alcohol. The yield of the dye was 21%, m.p. above 300° (with decompn.). The absorption maximum of the dye in ethanol lies at 642 mμ.

Found %: I 17.07. $C_{43}H_{33}O_2N_2I$. Calculated %: I 17.23.

(1-p-Methoxyphenyl-5,6-benzoquinoline-2)-(3-ethylbenzothiazole-2)-trimethinecyanine Perchlorate. A mixture of 0.25 g of p-methoxyphenylnaphthoquinaldinium iodide, 0.22 g of 2-β-acetanilinovinylbenzothiazole ethiodide and 1 ml of pyridine was heated at the boil for 90 minutes. The dye was isolated as the perchlorate by the addition of 5 ml saturated potassium perchlorate solution, 20 ml of water and 5 ml of alcohol, followed by heating to the boil and then cooling. The obtained carbocyanine was recrystallized from alcohol, after which it was chromatographed on aluminum oxide and extracted with an alcohol-benzene mixture. The absorption maximum of the dye in ethanol lies at 593 mμ.

Found %: Cl 6.32, 6.21. $C_{32}H_{27}O_5N_2SCl$. Calculated %: Cl 6.03.

(1-p-Methoxyphenyl-5,6-benzoquinoline-2)-(3,3,3-trimethylindolenine-2)-trimethinecyanine Perchlorate. A mixture of 0.55 g of p-methoxyphenylnaphthoquinaldinium iodide, 0.5 g of 2-β-acetanilinovinyldimethylindolenine methiodide and 3 ml of pyridine was heated at the boil in a paraffin bath for 80 minutes. The reaction product was treated repeatedly with hot water, dissolved in alcohol, and boiled with 10 ml of saturated potassium perchlorate solution. The dye was purified by chromatographing on aluminum oxide. The amount of substance obtained was 0.2 g (34%). M.p. 162-163°. Its absorption maximum in ethanol lies at 578 mμ.

Found %: Cl 6.27, 6.29. $C_{34}H_{31}O_5N_2Cl$. Calculated %: Cl 6.08.

(1-p-Methoxyphenyl-5,6-benzoquinoline-2)-(1-ethylquinoline-4)-monomethinecyanine Iodide. A mixture of 0.3 g of p-methoxyphenylnaphthoquinaldinium iodide, 0.4 g of quinoline ethiodide, 2 ml of anhydrous alcohol and 0.4 ml of saturated sodium alcoholate solution was heated for 30 minutes on the boiling water bath. The reaction product was treated with ether, dissolved in alcohol, and precipitated with potassium perchlorate solution. The dye was recrystallized from alcohol, m.p. 225-227° (with decompn.). The amount of dye obtained was 0.14 g (35%). The absorption maximum of the dye in ethanol lies at 575 mμ.

Found %: Cl 6.35. $C_{31}H_{25}O_5N_2Cl$. Calculated %: Cl 6.50.

(1-p-Ethoxyphenyl-7,8-benzoquinaldinium Perchlorate. A mixture of 2 g of p-ethoxyphenyl-α-naphthylamine, 1.4 g of paraldehyde, 6 ml of hydrochloric acid (d 1.19), 8 ml of benzene and 0.3 g of nitrobenzene was sealed in a glass tube and heated for 7 hours on the boiling water bath. The reaction product was treated with ether, dissolved in alcohol, and converted into the perchlorate. Recrystallization from alcohol gave 0.8 g (25%) of the salt, which melted at 218° (with decompn.).

Found %: Cl 8.59. $C_{22}H_{20}O_5NCl$. Calculated %: Cl 8.57.

Bis-(1-p-ethoxyphenyl-7,8-benzoquinoline-2)-trimethinecyanine Perchlorate. A mixture of 0.42 g of 1-p-ethoxyphenyl-7,8-benzoquinaldinium perchlorate, 0.3 g of ethyl orthoformate and 3 ml of pyridine was heated at the boil for 50 minutes in a paraffin bath. The obtained dye was precipitated with ether and recrystallized from aqueous alcohol. We obtained 0.14 g (19.4%) of dye with m.p. 281° (with decompn.). The absorption maximum of the carbocyanine in ethanol lies at 640 mμ.

Found %: Cl 4.99. $C_{45}H_{37}O_6N_2Cl$. Calculated %: Cl 4.80.

(1-p-Ethoxyphenyl-7,8-benzoquinoline-2)-(3-ethylbenzothiazole-2)-trimethinecyanine Perchlorate. A mixture of 0.41 g of 2-β-acetanilinovinylbenzothiazole ethiodide, 0.42 g of p-ethoxyphenylbenzoquinaldinium perchlorate, 2 ml of pyridine and several drops of acetic anhydride was heated at the boil for 40 minutes. The reaction product was treated with ether, and then with water. After recrystallization from aqueous alcohol the dark-violet crystals of the dye melted at 200° (with decompn.). The absorption maximum of the carbocyanine in ethanol lies at 596 mμ.

Found %: Cl 5.46. $C_{33}H_{29}O_5N_2SCl$. Calculated %: Cl 5.89.

(1-p-Ethoxyphenyl-7,8-benzoquinoline-2)-(1,3,3-trimethylindolenine-2)-trimethinecyanine Perchlorate. A mixture of 0.45 g of 2-β-acetanilinovinyldimethylindolenine methiodide, 0.42 g of p-ethoxyphenylbenzoquinaldinium perchlorate, 2.5 ml of pyridine and 0.5 ml of acetic anhydride was heated at slight boil for 60 minutes. The obtained dye was precipitated with ether, dissolved in alcohol, and converted into the perchlorate by treatment with saturated potassium perchlorate solution. After recrystallization from aqueous alcohol the carbocyanine melted at 208° (decompn.). The absorption maximum of the dye in ethanol lies at 584 mμ.

Found %: Cl 5.83. $C_{35}H_{33}O_5N_2Cl$. Calculated %: Cl 5.94.

(1-p-Ethoxyphenyl-7,8-benzoquinoline-2)-p-dimethylaminostyryl Perchlorate. A mixture of 0.42 g of p-ethoxyphenylbenzoquinaldinium perchlorate, 0.15 g of p-dimethylaminobenzaldehyde and 2 ml of pyridine was heated in a paraffin bath at the boil for 50 minutes. The styryl derivative was recrystallized from alcohol. The absorption maximum of the dye in ethanol lies at 546 mμ.

Found %: Cl 5.96. $C_{31}H_{29}O_5N_2Cl$. Calculated %: Cl 6.51.

We wish to thank V. N. Tolmachev for running the spectrophotometric measurements on the dyes.

SUMMARY

1. The reactions for the cyclization of p-methoxyphenyl-β-naphthylamine and p-ethoxyphenyl-α-naphthylamine in the presence of paraldehyde into N-arylquinaldinium derivatives were studied. In this connection the previously unknown quaternary salts 1-p-ethoxyphenyl-5,6-benzoquinaldinium iodide and 1-p-ethoxyphenyl-7,8-benzoquinaldinium perchlorate were obtained and their properties were studied.

2. Carbocyanines of both symmetrical and unsymmetrical structure were obtained on the basis of these salts, and also the isocyanine and styryl derivatives.

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DERIVATIVES OF ω-(2,4-DIAMINO-1,3,5-TRIAZYL-6)-ALKYLCARBOXYLIC ACIDS

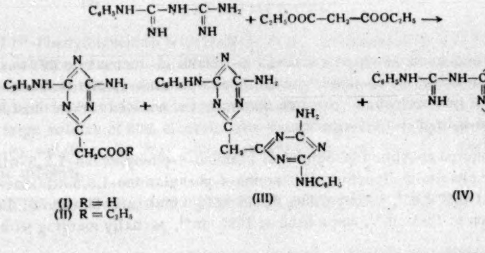
III. REACTION OF N'-PHENYLBIGUANIDE WITH MALONIC ESTER

S. V. Sokolovskaya, V. N. Sokolova and O. Yu. Magidson

As a continuation of previous work [1] we undertook the task of studying the reaction of N'-phenylbiguanide with malonic ester.

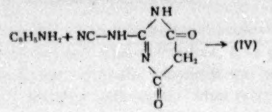
Whereas the reactions of urea [2], dicyandiamide [3] and guanidine [4] with malonic ester have been thoroughly studied, the reaction of the latter with biguanides is characterized by contradictory data in the literature. According to Rackmann [5] a pyrimidine compound is formed when biguanide is reacted with malonic ester, whereas Thurston [6] communicates that this reaction leads to the formation of a triazine and a small amount of a ditriazine; neither the constants of the obtained substances nor a proof of their structure are given in the mentioned papers. It is known that the condensation of biguanide with cyanoacetic ester leads to the formation of two compounds – one with a pyrimidine and the other with a triazine structure [7], while with acetylacetone biguanide forms a pyrimidine derivative [8].

We condensed N'-phenylbiguanide with malonic ester, the chloride of monoethyl malonate, the monopotassium salt of malonic ester and with cyanoacetic ester. As the result of condensing N'-phenylbiguanide with malonic ester, which was run in anhydrous alcohol medium in the presence of sodium alcoholate, we isolated four individual substances: 14.4% of 2-amino-4-phenylamino-1,3,5-triazine-6-acetic acid (I), 22.7% of its ethyl ester (II), 9.2% of methylene-bis-(2-amino-4-phenylamino-1,3,5-triazine-6) (III) and 34.7% of 2-phenylguanidino-4,6-dioxopyrimidine (IV).



The condensation of N'-phenylbiguanide with monoethyl malonyl chloride also led to the formation of the same four substances, but in somewhat different ratios, with a predominance of 2-amino-4-phenylamino-1,3,5-triazine-6-acetic acid and its ester.

The structure of (IV) was shown by the counter synthesis, proceeding from 2-cyanoamino-4,6-dioxopyrimidine and aniline in hydrochloric acid medium.



The infrared absorption spectra of (IV), obtained by the condensation of 2-cyanoamino-4,6-dioxopyrimidine with aniline (Fig. 1, Curve 1) and in the reaction of N'-phenylbiguanide with malonic ester (Fig. 1, Curve 2), coincide completely, as can be seen from Fig. 1.

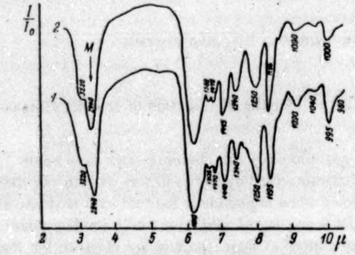
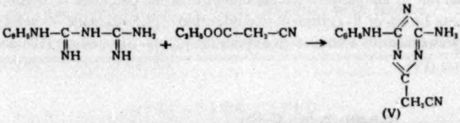


Fig. 1. Infrared absorption spectra of 2-phenylguanidino-4,6-dioxopyrimidine (in vaseline oil). M is the absorption band of vaseline oil. Explanation in the text.

The saponification of ethyl 2-amino-4-phenylamino-1,3,5-triazine-6-acetate (II) with alcoholic sodium hydroxide solution gave an acid with m.p. 100-102° (with decomposition), by analysis corresponding to 2-amino-4-phenylamino-1,3,5-triazine-6-acetic acid with one mole of water of crystallization. The monohydrate is an exceedingly unstable compound and easily loses carbon dioxide, being converted into 2-amino-4-phenylamino-6-methyl-1,3,5-triazine. The monohydrate was converted into the anhydrous 2-amino-4-phenylamino-1,3,5-triazine-6-acetic acid with m.p. 239-240° (with decompn.) only after long drying in a vacuum-desiccator over phosphoric anhydride.

The reaction of N'-phenylbiguanide with the monopotassium salt of malonic ester and with cyanoacetic ester confirmed the structure of 2-amino-4-phenylamino-1,3,5-triazine-6-acetic acid.



The nitrile group in 2-amino-4-phenylamino-1,3,5-triazine-6-acetonitrile (V) was saponified to the carboxyl group. The structure of the obtained 2-amino-4-phenylamino-1,3,5-triazine-6-acetic acid was shown by the decarboxylation of its monohydrate (based on the amount of evolved carbon dioxide and water) to give 2-amino-4-phenylamino-6-methyl-1,3,5-triazine.

In its shape the infrared absorption spectrum* of 2-amino-4-phenylamino-1,3,5-triazine-6-acetic acid (Fig. 2, Curve 1) is very close to the spectrum of 2-amino-4-phenylamino-1,3,5-triazine-6-carboxylic acid [1]. An intense band exists at 1650 cm^{-1}, corresponding to the antisymmetrical vibration of the triazine ring, an intense band in the region of 1385 cm^{-1}, and a band at 1630 cm^{-1}, partially merging with the minimum in the 1560 cm^{-1} region.

An anomaly in the position of the bands of C = O and the NH_2 group is observed in the spectrum of the triazineacetic acid (Fig. 2) and in the spectrum of 2-amino-4-phenylamino-1,3,5-triazine-6-carboxylic acid [1]. This is evidence that apparently there is also inner salt formation in the case of the triazineacetic acid. For the nitrile of this acid (V), where salt formation is excluded, as well as for the ester of 2-amino-4-phenylamino-1,3,5-triazine-6-carboxylic acid [1], the normal absorption band for the NH_2 group is observed at

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* A spectral study of the compounds obtained by us was made by Yu. N. Sheinker and coworkers, to whom we are most grateful.

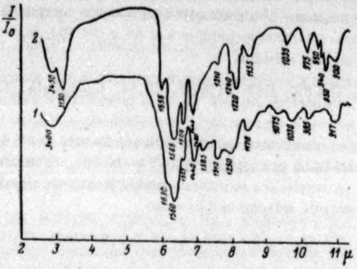

Fig. 2. Infrared absorption spectra of 2-amino-4-phenylamino-1,3,5-triazine-6-acetic acid (1) and 2-amino-4-phenylamino-1,3,5-triazine-6-acetonitrile (2). Diapason of 2-5 μ in polyfluorohydrocarbon, and 5-12 μ in vaseline oil.

1655 cm^{-1} and the absorption band, characteristic for the triazine ring, at 1565 cm^{-1} (Fig. 2, Curve 2).2-Amino-4-phenylamino-1,3,5-triazine-6-acetic acid with strong acids forms readily hydrolyzed salts and gives stable salts at the carboxyl group. The acid itself is rapidly decarboxylated in acid solutions, and as the hydrate, is an extremely unstable compound, evolving CO_2 even in the air. Other heterocyclic compounds, having a CH_2 COOH radical in the 2 position, show a similar behavior (for example, 2-pyridineacetic acid [9] and 8-caffeineacetic acid [10]).

The following derivatives of 2-amino-4-phenylamino-1,3,5-triazine-6-acetic acid were obtained: potassium and silver salts, methyl and ethyl esters, amide and hydrazide. In view of its exceeding instability the etherification of the acid with alcohols in the presence of concentrated sulfuric acid or dry hydrogen chloride is impossible; decarboxylation occurs even in the cold with the formation of 2-amino-4-phenylamino-6-methyl-1,3,5-triazine. The methyl ester was obtained from the silver salt of the acid and methyl iodide. The amide of 2-amino-4-phenylamino-1,3,5-triazine-6-acetic acid was obtained from the ethyl ester by treatment with alcoholic ammonia and by the hydration of 2-amino-4-phenylamino-1,3,5-triazine-6-acetonitrile with 87% sulfuric acid. The hydrazide was obtained from the ester by treatment with hydrazine hydrate.

EXPERIMENTAL

Condensation of N'-Phenylbiguanide With Malonic Ester. A mixture of 10 g of N'-phenylbiguanide, 9 ml of malonic ester and a solution of sodium alcoholate in alcohol (0.5 g of sodium metal in 20 ml of anhydrous alcohol) was heated at the boil under reflux for 5 hours. The alcohol was vacuum-distilled. The oily residue was thoroughly rubbed with 20 ml of 1N sodium hydroxide solution. The undissolved portion was filtered and recrystallized from a large volume of 80% alcohol. The first to deposit is methylene-bis-(2-amino-4-phenylamino-1,3,5-triazine-6), weight 1 g (9.2%): white crystalline substance with m.p. 274-275°, difficultly soluble in water and in organic solvents.

Found %: C 59.19, 58.79; H 4.88, 4.85; N 35.69, 35.85. $C_{19}H_{18}N_{10}$. Calculated %: C 59.07; H 4.66; N 36.27.

Partial evaporation of the alcoholic mother liquor gave as precipitate the ethyl ester of 2-amino-4-phenylamino-1,3,5-triazine-6-acetic acid, yield 3.5 g (22.7%): leaflets with m.p. 119-120°, readily soluble in alcohol, difficultly soluble in ether, and insoluble in water.

Found %: C 57.09, 57.08; H 5.43, 5.51; N 25.25. $C_{13}H_{15}O_2N_5$. Calculated %: C 57.14; H 5.49; N 25.64.

The alkaline filtrate was acidified with acetic acid to pH 6, the precipitate was filtered, and then it was dissolved in sodium bicarbonate solution. The undissolved portion was recrystallized from water. The weight of the obtained 2-phenylguanidino-4,6-dioxopyrimidine was 4.8 g (34.7%), m.p. 259-260°. A white crystalline substance, difficultly soluble in organic solvents.

Found %: C 53.86, 54.12; H 4.62, 4.57; N 28.25, 28.84. $C_{11}H_{11}O_2N_5$. Calculated %: C 53.88; H 4.49; N 28.57.

Acidification of the obtained bicarbonate solution with acetic acid to pH 4.5 gave 2-amino-4-phenylamino-1,3,5-triazine-6-acetic acid as a precipitate, yield 2 g (14.4%). After recrystallization from 75% alcohol, m.p. 239-240° (decompn.). A crystalline substance, soluble in sodium bicarbonate solution and in strong acids, and difficultly soluble in organic solvents and in water.

Found %: C 54.26, 54.08; H 4.61, 4.50; N 28.51. M 254 (titrated). $C_{11}H_{11}O_2N_5$. Calculated %: C 53.88; H 4.49; N 28.57. M 245.

Monoethyl Malonyl Chloride. To a suspension of 70 g of phosphorus pentachloride in 60 ml of anhydrous benzene was added in drops with stirring a solution of 36 g of monoethyl malonate in 15 ml of anhydrous benzene at 15-17° in 30 minutes. After all of the ester had been added the stirring was continued for another 15-20 minutes until the evolution of hydrogen chloride ceased. The solution was decanted from a small amount of phosphorus pentachloride, which was washed with benzene. The benzene and phosphorus oxychloride were vacuum-distilled from a Claisen flask with a 20-cm dephlegmator; the residual monoethyl malonyl chloride was vacuum-distilled at 72-73° (16 mm), yield 36 g (88%).

Condensation of N'-Phenylbiguanide With Monoethyl Malonyl Chloride. A solution of 5 g of N'-phenylbiguanide in 150 ml of anhydrous benzene was prepared by heating in a flask fitted with a Dean-Stark trap. Then 7 g of finely crushed fused potash was added, and with stirring a solution of 7.4 g of monoethyl malonyl chloride in 50 ml of anhydrous benzene was added in drops at 65° in 10-15 minutes, in which connection a precipitate was obtained. After all of the chloride had been added the temperature was raised to 80° and stirring was continued at benzene boil for 14 hours. The amount of water collected in the Dean-Stark apparatus was 0.5 ml. The obtained precipitate (A) was filtered, weight 14.3 g. The benzene filtrate was evaporated to dryness, and the residue was recrystallized from 75% alcohol. The yield of ethyl 2-amino-4-phenylamino-1,3,5-triazine-6-acetate was 2.7 g (37%), m.p. 119-120°.

To 14.3 g of precipitate (A) was added 100 ml of water, the mixture stirred well, and the insoluble portion (precipitate B) was filtered. The filtrate was acidified with acetic acid to pH 5, and the obtained precipitate was filtered and recrystallized from a large volume of 80% alcohol. The yield of 2-amino-4-phenylamino-1,3,5-triazine-6-acetic acid was 2 g (30%), m.p. 237-240° (decompn.). The mixed melting point with the triazine-6-acetic acid, obtained in the condensation of N'-phenylbiguanide with malonic ester, was not depressed.

Recrystallization of precipitate (B) from 80% alcohol gave first 0.4 g (8%) of methylene-bis(2-amino-4-phenylamino-1,3,5-triazine-6) with m.p. 274-275°, and then 1 g (15%) of 2-phenylguanidino-4,6-dioxopyrimidine with m.p. 259-260°.

2-Phenylguanidino-4,6-dioxopyrimidine. A mixture of 10 g of 2-cyanamino-4,6-dioxopyrimidine [3], 9.7 g of aniline hydrochloride and 100 ml of water was heated at the boil for 6 hours. The precipitate, the color of which toward the end of reaction became a light yellow, was filtered, and then washed with water and sodium bicarbonate solution. 2-Phenylguanidino-4,6-dioxopyrimidine was purified through the sodium salt, and then by fractional crystallization from a large volume of 80% alcohol to give 11 g (68.3%) of substance: thin leaflets with m.p. 259-260° (decompn.), soluble in dilute acids and caustic alkalies, difficultly soluble in alcohol, and insoluble in water. The mixed melting point with the 2-phenylguanidino-4,6-dioxopyrimidine, obtained in the reaction of N'-phenylbiguanide with malonic ester, was not depressed.

Found %: N 28.10, 28.27. $C_{11}H_{11}O_2N_5$. Calculated %: N 28.57,

Condensation of N'-Phenylbiguanide With the Potassium Salt of Monoethyl Malonate. To a warm solution of 25 g of N'-phenylbiguanide in 150 ml of anhydrous alcohol was gradually added with stirring a warm solution of 24 g of the potassium salt of monoethyl malonate in 100 ml of methanol and the reaction mass was stirred at the boil for 5 hours. The precipitate that deposited from the hot solution was filtered and recrystallized from a large volume of alcohol. The yield of the potassium salt of 2-amino-4-phenylamino-1,3,5-triazine-6-acetic acid was 18 g (45%); needles with m.p. 256-260°, readily soluble in water, and insoluble in cold alcohol.

Found %: K 13.89. $C_{11}H_{10}O_2N_5K$. Calculated %: K 13.78.

Three grams of the potassium salt of 2-amino-4-phenylamino-1,3,5-triazine-6-acetic acid was dissolved in water and acetic acid was added with cooling to pH 5. The precipitate was filtered and washed with water. For purification the obtained 2-amino-4-phenylamino-1,3,5-triazine-6-acetic acid was dissolved in sodium bicarbonate solution and the acid was precipitated from the solution by acidification with acetic acid to pH 5. The obtained acid crystallizes with 1 molecule of water. Weight 2 g, m.p. 100-102° (decompn.) (after effervescence the melt congeals and melts again at 178-180°).

Found %: C 50.13; H 4.98; N 26.64. $C_{11}H_{11}O_2N_5 \cdot H_2O$. Calculated %: C 50.15; H 4.94; N 26.64.

After long drying in a vacuum-desiccator over phosphoric anhydride the acid lost 1 mole of H_2O. The anhydrous 2-amino-4-phenylamino-1,3,5-triazine-6-acetic acid has m.p. 239-240° (decompn.). The mixed melting point with the acid, obtained in the reaction of N'-phenylbiguanide with malonic ester, failed to be depressed.

Silver Salt of 2-Amino-4-phenylamino-1,3,5-triazine-6-acetic Acid. To a solution of 5 g of the potassium salt of 2-amino-4-phenylamino-1,3,5-triazine-6-acetic acid in 20 ml of water was added with stirring a solution of 3 g of silver nitrate in 10 ml of water. After 30 minutes the obtained precipitate was filtered, washed with water, alcohol and ether, and dried at 100° for 2 hours. Yield 5.6 g (90%).

Found %: Ag 31.05, 30.91. $C_{11}H_{10}O_2N_5Ag$. Calculated %: Ag 30.64.

2-Amino-4-phenylamino-1,3,5-triazine-6-acetonitrile. A solution of 6 g of N'-phenylbiguanide and 5 ml of cyanoacetic ester in 25 ml of methanol was allowed to stand at room temperature for 30 hours. The obtained yellow precipitate was filtered and recrystallized from water. Yield of 2-amino-4-phenylamino-1,3,5-triazine-6-acetonitrile 3.8 g (50%): elongated colorless platelets with m.p. 152-153°, and soluble in alcohol, ether, hot water and dilute acids.

Found %: C 58.45, 58.64; H 4.55, 4.51; N 37.25, 37.26. $C_{11}H_{10}N_6$. Calculated %: C 58.40; H 4.42; N 37.17.

The hydrochloride of 2-amino-4-phenylamino-1,3,5-triazine-6-acetonitrile has m.p. 230-232°, and is easily hydrolyzed in water solutions.

Saponification of 2-Amino-4-phenylamino-1,3,5-triazine-6-acetonitrile. A mixture of 5 g of 2-amino-4-phenylamino-1,3,5-triazine-6-acetonitrile and 60 ml of 3% aqueous sodium hydroxide solution was heated on the boiling water bath for 1 hour. The precipitate went into solution. The solution was cooled and then treated with acetic acid to pH 5. Here 2-amino-4-phenylamino-1,3,5-triazine-6-acetic acid was obtained in a precipitate, which was filtered, then dissolved in sodium bicarbonate solution, and precipitated again by the addition of acetic acid to pH 5. The precipitate was filtered, washed with water, alcohol and absolute ether, and then placed in a vacuum-desiccator over phosphoric anhydride. Yield of 2-amino-4-phenylamino-1,3,5-triazine-6-acetic acid 3.5 g (65%), m.p. 100° (decompn.) (after effervescence the melt congeals and melts again at 179-181°).

After long drying in the vacuum-desiccator over phosphoric anhydride, m.p. 237-240° (decompn.). The mixed melting point with the acid, obtained in the condensation of N'-phenylbiguanide with malonic ester, was not depressed.

Saponification of Ethyl 2-Amino-4-phenylamino-1,3,5-triazine-6-acetate. A mixture of 0.5 g of ethyl 2-amino-4-phenylamino-1,3,5-triazine-6-acetate and 5 ml of 2.5% alcoholic sodium hydroxide solution was heated at the boil for 3 hours. Within 30 minutes a precipitate began to deposit. The sodium salt of 2-amino-4-phenylamino-1,3,5-triazine-6-acetic acid was filtered, washed with anhydrous alcohol, dissolved in water, and the acid precipitated by the addition of acetic acid to pH 5. The precipitate was filtered, washed with water, anhydrous alcohol and absolute ether, and then placed in a vacuum-desiccator over phosphoric anhydride. The yield of the 2-amino-4-phenylamino-1,3,5-triazine-6-acetic acid monohydrate was 0.36 g (80%), m.p. 102-105° (after effervescence it congeals and melts at 180-181°).

Decarboxylation of 2-Amino-4-phenylamino-1,3,5-triazine-6-acetic Acid. 2-Amino-4-phenylamino-1,3,5-triazine-6-acetic acid monohydrate (0.4319 g) was heated in a bath for 1 hour at 130-150°. The substance melted at 100° with the evolution of CO_2 bubbles.

Found: weight of residue 0.338 g; CO_2 0.065 g; H_2O 0.0289 g. $C_{11}H_{11}O_2N_5 \cdot H_2O$. Calculated: weight of 2-amino-4-phenylamino-6-methyl-1,3,5-triazine 0.330 g; CO_2 0.072 g; H_2O 0.0295 g.

The residue was recrystallized from dilute methyl alcohol. Weight 0.28 g, m.p. 180-182°. The mixture with the 2-amino-4-phenylamino-6-methyl-1,3,5-triazine, obtained from N'-phenylbiguanide and acetic anhydride, had m.p. 181-182°.

Methyl 2-Amino-4-phenylamino-1,3,5-triazine-6-acetate. A solution of 1 g of methyl iodide in 10 ml of methanol was added in drops and with stirring in 15 minutes to a fine suspension of 2 g of the silver salt of 2-amino-4-phenylamino-1,3,5-triazine-6-acetic acid in 40 ml of methanol at 22°. The reaction mass was stirred at room temperature for 8 hours and then allowed to stand overnight. The next day the gray-yellow precipitate of silver iodide was filtered. Weight 1.65 g. The alcohol was distilled from the filtrate in vacuo; the residual oily mass after solidification was recrystallized from 75% methyl alcohol. Yield of methyl 2-amino-4-phenylamino-1,3,5-triazine-6-acetate 0.6 g (43%): elongated microscopic platelets with m.p. 121-122°, readily soluble in alcohol, soluble in ether, and insoluble in water.

Found %: C 55.88, 55.99; H 5.24, 5.06; N 27.18. $C_{12}H_{33}O_2N_5$. Calculated %: C 55.59; H 5.02; N 27.02.

2-Amino-4-phenylamino-1,3,5-triazine-6-acetamide. a) A mixture of 0.2 g of ethyl 2-amino-4-phenylamino-1,3,5-triazine-6-acetate and 10 ml of 19% ammonia solution in methyl alcohol was shaken for 15-20 minutes until the precipitate dissolved and then it was allowed to stand at room temperature for 19 days. The precipitate that deposited on cooling the solution was filtered and recrystallized from 75% alcohol (1 : 25). Yield of 2-amino-4-phenylamino-1,3,5-triazine-6-acetamide 0.11 g (61%): tetrahedral prisms with m.p. 203-204°.

Found %: C 54.08, 54.74; H 5.15, 5.01; N 34.54, 34.15. $C_{11}H_{12}ON_6$. Calculated %: C 54.09; H 4.92; N 34.43.

b) A mixture of 1 g of 2-amino-4-phenylamino-1,3,5-triazine-6-acetonitrile and 5 ml of 87% sulfuric acid was heated at 65-70° for 2 hours. Then the whole mass was poured into 60 ml of ice water. The obtained precipitate was filtered, washed with water, and rubbed with sodium bicarbonate solution. The undissolved portion was filtered, washed with water, and recrystallized from 75% methyl alcohol (1: 25). The yield of the amide was 0.5 g (46.3%), m.p. 203-204°. The mixed melting point with the 2-amino-4-phenylamino-1,3,5-triazine-6-acetamide, obtained from the ethyl ester, was not depressed.

Hydrazide of 2-Amino-4-phenylamino-1,3,5-triazine-6-acetic Acid. A warm solution of 0.4 g of ethyl 2-amino-4-phenylamino-1,3,5-triazine-6-acetate in 3 ml of alcohol was treated with 1 ml of hydrazine hydrate and the mixture was allowed to stand. The next day the obtained precipitate was filtered and recrystallized from a large volume of alcohol. The yield of the hydrazide of 2-amino-4-phenylamino-1,3,5-triazine-6-acetic acid was 0.3 g (80%): needles with m.p. 215-216°, difficultly soluble in alcohol, and insoluble in water and ether.

Found %: C 50.88, 51.12; H 5.23, 5.19; N 38.1. $C_{11}H_{13}ON_7$. Calculated %: C 50.96; H 5.02; N 37.80.

SUMMARY

1. The reaction of N'-phenylbiguanide with malonic ester and with the chloride of malonic monoester gave 2-amino-4-phenylamino-1,3,5-triazine-6-acetic acid (14.4%), the corresponding ester (22.7%), methylene-bis-(2-amino-4-phenylamino-1,3,5-triazine-6) (9.2%) and 2-phenylguanidino-4,6-dioxopyrimidine (34.7%).

2. The reaction of N'-phenylbiguanide with the monopotassium salt of malonic ester led to the formation of 2-amino-4-phenylamino-1,3,5-triazine-6-acetic acid.

3. The reaction of N'-phenylbiguanide with cyanoacetic ester gave 2-amino-4-phenylamino-1,3,5-triazine-6-acetonitrile, the saponification of which gave 2-amino-4-phenylamino-1,3,5-triazine-6-acetic acid.

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POLAROGRAPHIC STUDY OF 2,3-DERIVATIVES OF 1,4-NAPHTHOQUINONE

I. F. Vladimirtsev and A. G. Stromberg

Many natural derivatives of naphthoquinone manifest biological activity (juglone, plumbagin, javanicin, vitamin K, etc.) [1]. In addition, due to their quinoid structure the naphthoquinones represent extremely reactive substances, in which a sharp change in properties appears as a function of the character and location of substituents. These properties of the naphthoquinones are the reason for the many investigations in this field [2-5].

In the present investigation the ability of 2,3-derivatives of 1,4-naphthoquinone to be reduced at the dropping mercury electrode was studied for the purpose of examining the reciprocal effect exerted by atoms and groups in the molecules of quinones.

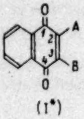
Most organic compounds show irreversible reduction at the dropping mercury electrode. Quinones are one of the few classes of organic compounds that show reversible reduction at the dropping mercury electrode [6].

The polarographic method characterizes the oxidation-reduction properties of the quinone-hydroquinone system, which depend on the chemical structure of both the quinone and hydroquinone. The value of the reversible half-wave potential ($\varphi_{1/2}$) characterizes the influence of the atoms and groups in a molecule on its relative ability to undergo reduction. The latter changes with change in the "fine" structure of the molecule.

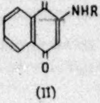
Numerous studies exist [7-10] on the determination of the oxidation-reduction potentials (φ_0) of quinones potentiometrically. Relatively few studies are known on the polarographing of quinones. Thus, Smith [11] studied about 20 quinones in buffered alcohol-water solutions. McCawley [12] investigated a number of naphthoquinones. Of the other investigations we will mention the study of citrinin [13], phthiocol [14], metabolites of molds and related quinones [15], anthraquinone derivatives [16, 17] and a study of the photochemical change of quinones [18]. The work of Beiles [19, 20] on a study of 17 different anthraquinones, naphthacenequinone, etc. (1,4-naphthoquinone was included among them) also deserves attention. Some benzoquinone derivatives are investigated in the work of A. G. Stromberg [21], and here the values for the shift of the half-wave potentials by various substituents are shown.

An examination of even these few data indicates the usefulness of the polarographic method in studying the structure and properties of quinones. Consequently, it could be assumed that a study of the half-wave potentials of the 49 naphthoquinone derivatives synthesized by us (16 of them are new), differing from each other in the character of the substituents in the 2,3 positions of the quinone ring, would in some measure reflect the nature of the reciprocal effect exerted by the atoms and groups in a molecule.

Based on the number and character of the substituents, the naphthoquinone derivatives synthesized by us can be divided into 5 groups.



(I*)



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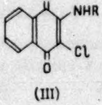

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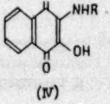

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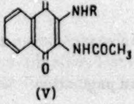

(V)

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* The figure under the formula indicates the group to which a given substance belongs.

A and B are hydrogen, hydroxyl, methoxy and acetoxy, and R is hydrogen, β-naphthyl, acetyl, phenyl and phenyl with substituents (chlorine, carboxyl, sulfamido, nitro and methoxy) in the ortho- and para-positions.

The compounds in each group were obtained by the condensation of the corresponding starting substance for a given group and the substituted amine in either alcohol or acetic acid medium.

All of the synthesized substances were carefully purified by repeated recrystallization; for the known substances the melting points corresponded to the literature data.

Method of Operation. A visual polarograph designed by the Ural Branch of the Academy of Sciences [22] was used for the polarographic study of the naphthoquinone derivatives.

A saturated calomel semielement served as the anode. The cathode was a dropping-mercury electrode (drop. Hg el.), immersed in the investigated solution. The dissolved atmospheric oxygen was removed from the solution by the passage of purified hydrogen from a Kipp apparatus for 10-15 minutes. To obtain distinctly comparable results we used buffer solutions for all of the groups of naphthoquinones.

In view of the fact that many of the quinones proved to be difficultly soluble in alcohol at 25°, we came to work with water-alcohol solutions, containing 75% (by volume) alcohol.

As an indifferent electrolyte we used two buffer solutions: an acetate buffer solution – a mixture of 0.1N CH_3COOH and 0.1N CH_3COONa (a), and an ammoniacal buffer solution – a mixture of 0.1N NH_4OH and 0.1N NH_4Cl (b).

To elucidate the influence of the solution pH on the magnitude of $\varphi_{1/2}$ and for the purpose of mutual verification the half-wave potentials of nearly all of the compounds studied in this paper were measured in both of the indicated buffer solutions.

The determinations were run without the addition of gelatin, since maxima, distorting the polarograms, were absent for the quinones. In most cases the experiments were run at a quinone concentration of $1.0 \cdot 10^{-3}$ mmole; for difficultly soluble compounds the experiments were run with a saturated solution of the quinone (arbitrary concentration).*

The current of the ground (inoculation current) was slight at the galvanometer sensitivities employed in the experiments.

For plotting the curve a determination was considered satisfactory if the values of the half-wave potentials in two parallel experiments did not differ by more than ± 2mV, and if such was not the case the determination was repeated until comparable data were obtained.

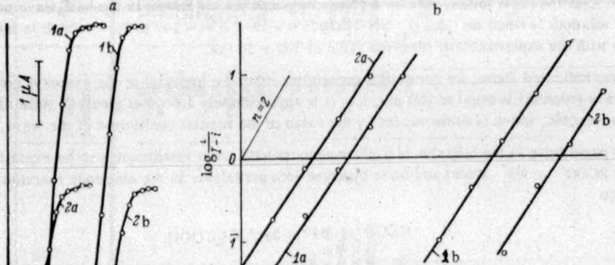

Fig. 1a. Polarograms of compounds 10 and 30 in two buffer solutions. 1) for compound 10, 2) for compound 30, a) acetate buffer, b) ammoniacal buffer. Fig. 1b. Wave plots of compounds 10 and 30 in the semilogarithmic coordinates $\log\frac{i}{I-i}$ and $(-\varphi)$ in the two buffer solutions. (Designations the same as for Fig. 1a).

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* Some of the substances proved to be practically insoluble and their polarograms could not be taken (these were 2-p-nitroanilino-1,4-naphthoquinone; 2-N'-sulfanilylamido-3-chloro-1,4-naphthoquinone; 2-p-chloroanilino-3-chloro-1,4-naphthoquinone; p,p'-(3-chloronaphthoquinonoyl-2-diaminodiphenyl sulfone; and the sulfamido analog of compound 46).

In different experiments the characteristic of the capillary under the influence of the half-wave potential varied in the limits 1.46-1.49 $mg^{2/3}$ $sec.^{-1/2}$. For each substance the polarogram and graph in semilogarithmic coordinates were constructed on the basis of the experimental data (Fig. 1).

Three characteristics were calculated for each wave – the half-wave potential ($\varphi_{1/2}$), the angular coefficient (B) and the diffusion current constant (K_D) (when the solution concentration of the^2 quinone was known).

With small exception, the investigated 1,4-naphthoquinone derivatives gave distinct polarograms and straight lines on the semilogarithmic plot. The slope of the latter corresponded to a reversible electrode process with participation of two electrons in the reduction process.

A comparison of the half-wave potential values for the same naphthoquinone in the two buffer solutions revealed that the half-wave potentials of quinones depend on the pH of the solution; in this connection for the quinones, not reacting with the electrolyte, the difference in the half-wave potentials in the two buffer solutions ($\Delta \varphi$) was equal to 150 ± 10 mV (Table 1). In the case of the oximino derivatives this difference, with all of the other conditions constant, corresponded to the greater value 200 ± 10 mV (compounds 5, 7, 8, 27-38).

Subsequently, to study the influence of substituents on the value of the half-wave potential of a substituted naphthoquinone we used the values of the half-wave potentials in the acetate buffer, since more distinct polarographic curves are obtained in it. Measuring the pH with a glass electrode gave for the acetate and ammoniacal buffers a pH of 6.2 and 8.7, respectively, i.e. the pH of the two buffer solutions differed by 2.5 units.

A difference of 150 mV in the half-wave potentials for the compounds without either the OH or the COOH group can be explained in the following manner. The electrode process for the reduction of naphthoquinones at a dropping mercury electrode is a reversible process in both of the buffer solutions, as follows from the angular coefficient of the wave in accord with the equation

$$R + 2H^+ + 2e \rightleftarrows RH_2. \tag{1}$$

From this we obtain for the reversible half-wave potential the expression • [23]

$$\varphi_{1/2} = \varphi_0 - 59\text{pH}, \tag{2}$$

where φ_0 is the normal oxidation-reduction potential of the system (at pH 0).

From Equation (2) it follows that for a given compound the difference in the half-wave potentials in the two buffer solutions is equal to: $\Delta \varphi_{1/2} = -59\,\Delta\text{pH} = -59 \cdot 2.5 = -147$ mV, which is found to be in good agreement with the experimentally observed value of 150 ± 10 mV.

As was indicated above, for compounds containing either the hydroxyl or the carboxyl group, the shift in the half-wave potential is equal to 220 mV, i.e. it is approximately 1.5 times greater. Here also the electrode process is reversible, which is demonstrated by the value of the angular coefficient of the wave.

This peculiarity in the behavior of naphthoquinones with given substituents can be explained if we assume that either $RCOO^-$ or RO^- anions and three hydrogen ions participate in the electrode reaction, in accord with the equation

$$RCOO^- + 3H^+ + 2e \rightleftarrows RH_2COOH, \tag{3}$$

From this equation we obtain the following expression for the reversible half-wave potential

$$\varphi_{1/2} = \varphi_0 - 87\text{pH}. \tag{4}$$

• For simplicity we will assume here that the diffusion coefficients and the activity coefficients for the oxidized and reduced forms of a given compound are respectively equal.

TABLE 1

Summary Table of the Polarographic Study Results

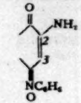
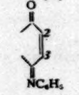
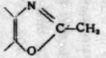
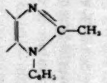
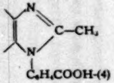
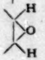
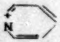
Compound Nos.	Substituents in the formulas of the naphthoquinones		Buffer solution "a" (acetate)			Buffer solution "b" (ammoniacal)			$\Delta\varphi = \varphi_{1/2}(b) - \varphi_{1/2}(a)$	$\varphi_{1/2}(a) - (-124)$	Literature on the synthesis of the compounds
	in the 2 position	in the 3 position	K_D	B	$\varphi_{1/2}$(mV)	K_D	B	$\varphi_{1/2}$(mV)			
				Group I							
1	H	H	1.74	0.035	—124	2.26	0.030	—278	154	0	[26]
2	Cl	OH	2.00	0.034	—342	2.04	0.035	—574	232	218	[27, 8]
3	OH	OH	1.63	0.035	—332	1.42	0.035	—542	210	208	[28]
4	OH	H	2.26	0.035	—294	2.30	0.036	—523	229	170	[29]
5	OCH_3	H	2.62	0.037	—249	2.64	0.035	—398	149	125	[29]
6	CH_3	H	2.66	0.036	—205	2.86	0.036	—346	141	81	[8]
7	Cl	$OCOCH_3$	2.79	0.038	—167	2.58	0.034	—320	154	43	[25]
8	Cl	Cl	2.88	0.041	—120	Solution turns brown rapidly				— 4	[30, 31]
9	Cl	H	3.05	0.038	—112	The same				— 12	[32]
				Group II							
10	NH_2	H	2.10	0.036	—345	2.20	0.035	—493	148	221	[8]
11	NHC_6H_5	H	1.76	0.034	—323	1.74	0.035	—475	152	199	[26]
12	$NHC_{10}H_7$-β	H	Satd. soln	0.035	—307	—	—	—	—	183	×
13	NHC_6H_4COOH-(4)	H	Satd. soln	0.089	—290	—	0.064	—461	171	166	[33]
14	$NHC_6H_3Cl_2$-(2,4)	H	1.45	0.034	—277	—	—	—	—	153	×
15	$NHC_6H_4SO_2NH_2$-(4)	H	Satd. soln	—	—273	—	—	—423	150	149	[44]
16			2.08	0.036	—237	1.98	0.036	—399	162	113	[34]
17			1.69	0.036	— 85	1.64	0.036	—236	151	— 39	[34]

TABLE 1 (Continuation)

Compound Nos.	Substituents in the formulas of the naphthoquinones		Buffer solution "a" (acetate)			Buffer solution "b" (ammoniacal)			$\Delta\varphi = \varphi_{1/2}(b) - \varphi_{1/2}(a)$	$\varphi_{1/2}(a) - (-124)$	Literature on the synthesis of the compounds
	in the 2 position	in the 3 position	K_D	B	$\varphi_{1/2}$(mV)	K_D	B	$\varphi_{1/2}$(mV)			
	Group III										
18	NH_2	Cl	2.66	0.035	−350	2.74	0.034	−505	155	226	[25]
19	$NHC_6H_4OCH_3$-(4)	Cl	Satd. soln	0.036	−267	—	—	—	—	143	[35]
20	NHC_6H_5	Cl	1.56	0.031	−245	1.53	0.028	−395	150	121	[35]
21	$NHC_{10}H_7$-β	Cl	1.32	0.031	−243	—	0.034	−392	149	119	[36]
22	NHC_6H_4COOH-(4)	Cl	Satd. soln	0.032	−217	—	0.035	−398	181	93	[36]
23	$NHC_6H_4NO_2$-(4)	Cl	Satd. soln.	0.034 0.058	−174 −670	—	—	−325 −695	151	50	[35]
24	$N(C_2H_5)C_6H_5$	Cl	2.45	0.035	−152	3.35	0.034	−305	153	28	[36]
25	$NHCOCH_3$	Cl	2.32	0.035	−135	2.15	0.035	−284	149	11	[25]
26	$N(COCH_3)C_6H_5$	Cl	1.86	0.035	−108	1.77		−265	157	− 14	[24]
	Group IV										
27	NH_2	OH	2.28	0.035	−383	1.80	0.034	−557	174	259	[37]
28	$NHC_6H_4OCH_3$-(4)	OH	1.70	0.033	−341	—	—	—	—	217	×
29	$NHC_6H_4OCH_3$-(2)	OH	1.88	0.034	−327	—	—	—	—	204	×
30	NHC_6H_5	OH	2.37	0.033	−324	2.25	0.032	−585	210	200	[28]
31	$NHC_6H_4NO_2$-(4)	OH	Satd. soln	—	−325 −680	—	—	—	—	201	×
32	$NHC_6H_4NO_2$-(3)	OH	Satd. soln	—	−325 −590	—	—	—	—	201	×
33	NHC_6H_4Cl-(4)	OH	Satd. soln	0.038	−324	—	—	—	—	200	×
34	NHC_6H_4Cl-(2)	OH	Satd. soln	0.035	−325	—	—	—	—	201	×
35	$NHC_6H_3Cl_2$-(2,4)	OH	Satd. soln	0.033	−323	1.60	0.034	−548	225	199	×
36	NHC_6H_4COOH-(4)	OH	Satd. soln	0.041	−315	1.35	0.033	−532	217	191	×
37	$NHC_6H_4SO_2NH_2$-(4)	OH	Satd. soln	0.027	−315	1.60	0.034	−540	225	191	×
38	$N(C_2H_5)C_6H_5$	OH	1.33	0.034	−298	1.59	0.033	−517	219	174	× [40]

TABLE 1 (Continuation)

Compound Nos.	Substituents in the formulas of the naphthoquinones		Buffer solution "a" (acetate)			Buffer solution "b" (ammoniacal)			$\Delta\varphi = \varphi_{1/2}(b) - \varphi_{1/2}(a)$	$\varphi_{1/2}(a) - (-124)$	Literature on the synthesis of the compounds
	in the 2 position	in the 3 position	K_D	B	$\varphi_{1/2}$(mV)	K_D	B	$\varphi_{1/2}$(mV)			
				Group V							
39	NH_2	$NHCOCH_3$	1.73	0.034	−354	1.67	0.037	− 508	154	230	[8]
40	NHC_6H_5	$NHCOCH_3$	1.75	0.032	−280	1.78	0.033	− 436	156	156	[24]
41	NHC_6H_4COOH-(4)	$NHCOCH_3$	Satd. soln	0.026	−253	—	—	—	—	129	×
42	$NHC_6H_4SO_2NH_2$-(4)	$NHCOCH_3$	Satd. soln	0.032	−238	—	—	—	—	114	×
43	$N(C_2H_5)C_6H_5$	$NHCOCH_3$	—	—	(−200)	—	—	—	—	76	×
44			Satd. soln	0.031	−229	—	—	—	—	105	[24]
45			1.90	0.060	−410	—	—	—	—	286	[24]
46			1.79	0.051	−370	—	—	—	—	246	×
47	ONa	NO_2	—	—	−365	—	—	− 535	170	241	[38]
48			2.23 1.90	0.075 0.140	−755 (I) −1048 (II)	2.23 —	0.079 —	− 755 −1078	0 —	— —	[28, 3, 8]
49		$\overline{O}$	1.69	0.035 0.040	−395 (I) −1237 (II)	1.78	0.035 0.042	− 570 −1380	175	—	[39]

Remarks. The compounds, synthesized for the first time, are designated by a cross (x). The half-wave potentials are given relative to the saturated calomel electrode (satd. cal. el.).

The difference in the half-wave potentials of a given compound in the two buffer solutions discussed here is $\Delta \varphi_{1/2} = -87 \cdot \Delta pH = -87 \cdot 25.5 = -217.5$ mV, which is found to agree with the observed experimental value 220 ± 10 mV.

This explanation will be valid if it is assumed that the degree of dissociation shown by the carboxyl and hydroxyl derivatives of naphthoquinones is considerably greater than that of the corresponding hydroquinones.

The validity of Equation (2) can be shown by comparing the experimental data obtained by Fieser for the normal electrode potentials of a number of naphthoquinones with the values of these potentials calculated on the basis of formula (2), proceeding from our experimental data for the half-wave potentials.

The results of these calculations for a number of naphthoquinones in acetate buffer solution are given in Table 2.*

TABLE 2

Compound Nos.	1	3	4	5	6	8	9	10	11	17
$\varphi_{1/2}$(mV)(satd.cal.el)	−124	−332	−294	−249	−205	−112	−120	−345	−323	− 85
φ_0(calc.)(normal hydrogen electrode)	492	284	322	367	411	504	496	271	293	532
φ_0(Fieser)(normal hydrogen electrode)	483	288	356	356	408	508	494	271	285	531

From the data in Table 2 it can be seen that in all cases good agreement is observed between the experimental and calculated values for the normal electrode potential.

As a result, it is possible to calculate with suitable accuracy from the experimental data for the normal electrode potentials of naphthoquinones the values of the half-wave potentials of those compounds for which experimental data are lacking, and to make the reverse calculation. We make use of such calculated data at times below.

DISCUSSION OF RESULTS

All of the 49 1,4-naphthoquinone derivatives studied by us with substituents in the 2,3 positions of the quinoid ring are arranged by groups of related compounds (I-V) in Summary Table 1. From the data in Table 1 it can be seen that most of the compounds show reversible reduction with participation of two electrons (compounds 13, 45, 46, 47 and 48 are exceptions). The values of the half-wave potentials ($\varphi_{1/2}$) of these compounds in acetate buffer solution (a) are found to range from −100 to 400 mV.

An examination of the general picture of the influence of various substituents on the value of the half-wave potential when compared with the unsubstituted 1,4-naphthoquinone (No. 1) already clearly shows that the presence of some substituents causes the half-wave potential to shift toward more negative values, i.e. it makes reduction of the compound difficult; on the other hand, the presence of other substituents facilitates reduction. The latter occurs only for the monochloronaphthoquinone (No. 9), dichloronaphthoquinone (No. 8), and also for compounds 17 and 26. Of the substituents, making reduction difficult, the greatest influence is shown by the hydroxyl group (Nos. 3 and 4) and the amino group (No. 10), and the smallest influence is shown by the acetamino group (No. 25).

In the 2-amino-3-chloronaphthoquinone group (Nos. 18-26) the radicals (R), replacing the hydrogen atom on the amino group, can be arranged in the following order of increasing influence on the ability of the quinone to be reduced.

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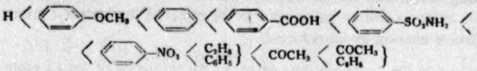
* In these calculations it should be kept in mind that the normal electrode potentials were calculated by Fieser relative to the normal hydrogen electrode (n. h. e.), while our experimental data for the half-wave potentials were calculated relative to the saturated calomel electrode.



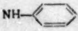
A similar rule is also clearly shown in the 2-aminonaphthoquinone (Nos. 10-17) and 2-amino-3-acetaminonaphthoquinone (Nos. 39-43) groups. In contrast to these groups of compounds, in the 2-amino-3-hydroxynaphthoquinone group (Nos. 27-28) a weakening effect of the hydroxyl group on the influence of the other substituents in the benzene ring is observed. A hydroxyl group in the 3 position reduces the influence of the COOH and SO_2NH_2 groups (Nos. 36 and 37), found in the para-position of the phenyl radical, and as it were eliminates the influence of Cl atoms and of the NO_2 group in the phenyl radical (Nos. 33, 34, 35, and 31 and 32).

The half-wave potentials of 11 of the compounds in this group are found in the narrow interval of −300 to −340 mV.

From the data in Table 3 it can be seen that if the values of the half-wave potentials of the amino compounds (Group II) are compared with those of the corresponding aminochloro compounds (Group III), then the presence of a chlorine atom in the 3 position of the quinoid ring causes an average reduction of 71 mV in the value of the half-wave potential (except for the compounds with an NH_2 group).

TABLE 3

Influence of Chlorine as a Second Substituent on the Half-Wave Potential

Substituents	NH_2	NHC_6H_5	NH– –COOH	NH––SO_2NH_2	$NHCOCH_3$
$\varphi_{1/2}$ (Group II) . . .	−345	−323	−290	−275	(−200)*
$\varphi_{1/2}$ (Group III) . . .	−350	−248	−217	−(204)**	−135
$\Delta\varphi_{Cl} = \varphi_{1/2\,(II)} - \varphi_{1/2\,(III)}$	+ 5	− 75	− 73	− 71	− 65

$$\underbrace{\qquad\qquad\qquad\qquad}_{\text{Average } -71 \text{ mV}}$$

---

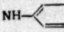
* The value of $\varphi_{1/2}$ was obtained by calculation from $\varphi_0 = 416$ mV (according to Fieser) [8].

** The half-wave potential was calculated with the average effect of the $SO_2\ NH_2$ group (from two compounds of two other groups, namely Nos. 14 and 43) taken equal to +44 mV: $\varphi_{1/2} = \varphi_{1/2\,No.\,20} - \Delta\varphi_{1/2\,SO_2NH_2} = -248 + 44 = -204$ mV.

In a similar manner, a comparison of the amino compounds (Group II) with the aminoacetamino compounds (Group V) reveals that the presence of the acetamino group reduces the half-wave potential by an average of 39 mV (Table 4).

TABLE 4

Influence of the Acetamino Group as a Second Substituent on the Half-Wave Potential

Substituents	NH_2	NHC_6H_5	NH– –COOH	NH––SO_2NH_2
$\varphi_{1/2}$ (Group II) . . .	−345	−323	−290	−275
$\varphi_{1/2}$ (Group V) . . .	−354	−280	−253	−238
$\Delta\varphi = \varphi_{1/2}\ (II) - \varphi_{1/2}\ (V)$	+ 9	− 43	− 37	− 37

$$\underbrace{\qquad\qquad\qquad\qquad}_{\text{Average } -39 \text{ mV}}$$

It is interesting to mention that the influence of the acetamino group as a second substituent is similar to the influence of the chlorine atom,* in contrast to the effect of the hydroxyl group, which serves to distort the picture of the influence exerted by substituents.

It is understood that the found average values of the influence of the Cl atom and $NHCOCH_3$ group on the half-wave potential are approximate. However, the found rule might prove useful for an orienting evaluation of the half-wave potentials of similar compounds in the corresponding groups.**

Thus, for example, for compound No.43 $\varphi_{1/2} = \varphi_{1/2\,\text{No.24}} + (-34) = -(152 + 34) = -186$ mV. From experiment we obtained only an approximate value of the half-wave potential of this compound −200 mV, since we were unable to separate the compound completely from the starting product (No. 25). It is possible to assume that the obtained calculated value −186 mV is more accurate.

As a result, a comparison of the half-wave potentials of the compounds in these three groups (II, III, V) revealed that it is possible to predict the values of the half-wave potentials of analogous compounds in another group (except for the compounds with an unsubstituted amino group, Nos. 10, 18 and 27).

Consequently, for the studied compounds the influence shown by the second substituent is additive. For a number of other compounds the additive influence of substituents is absent, for example, Nos. 4, 9 and 2; Nos. 1, 4 and 3; and Nos. 9, 7 and 2-acetoxyl-1,4-naphthoquinone ($\varphi_{1/2} = -141$ mV, at $\varphi_0 = 475$ mV [7, 8]). In the first case the half-wave potential for compound 2 proves to be more negative than for compounds 4 and 9, each of the latter having only one substituent. In the second case the influence shown by one and by two OH groups is unequal. And, finally, for the acetoxychloronaphthoquinone the half-wave potential is more negative than for the monosubstituted compounds.

For the cyclic derivatives (Nos. 44-46), obtained from the compounds Nos. 25, 40 and 41, the half-wave potentials, as can be seen from the data in Table 1, proved to be much more negative than for the original compounds. Their polarograms and semilogarithmic plots have a distorted appearance, which testifies to the irreversible nature of the reduction process (Nos. 45 and 46).

We will examine some other compounds. Nitro compounds 23, 31, 32 and 47 are interesting for the following reasons. If the nitro group is found in the phenyl radical, then the polarogram has two waves (Fig. 2). The first of them corresponds to the reduction of the quinoid grouping (−175 mV for No. 23), and the second corresponds to the reduction of the nitro group. The height of the second wave is approximately 3 times that of the first and, consequently, corresponds to the loss of 6 electrons (for compounds Nos. 23, 31 and 32). This means that the reduction proceeds to the amino group: $NO_2 + 6H^+ + 6e \rightarrow NH_2 + 2H_2O$. In this connection the value of the half-wave potential lies in the limits of −500 to −700 mV. In the case where the nitro group is found in the quinoid ring there appears only one wave with $\varphi_{1/2} = -356$ mV. Its height is the same as the sum of the heights of the waves in the previous case, which indicates that the reduction of the two groupings is superimposed in the examined case (No. 47).

Naphthoquinone oxide (48), as was to be expected on the basis of its structure, is reduced in an entirely different manner from the quinones. Two waves with potentials −755 and −1048 mV are found on the polarogram (Fig. 3). Of them only the second wave shows slight reaction when the pH is changed. This suggests that the reduction process is irreversible. It may be assumed that the first wave corresponds to the reduction of one CO group, and the second corresponds to the reduction of the second group.

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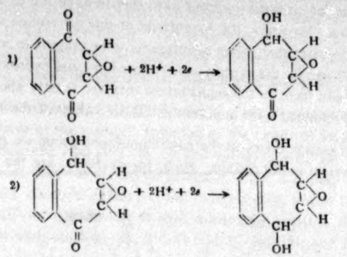
* Fries and Billig [24] mention the great similarity in the chemical behavior and physicochemical properties of the aminochloro- and aminoacetaminonaphthoquinone groups.

** This is especially valuable in those cases where the obtained compounds are practically insoluble in a given buffer solution.



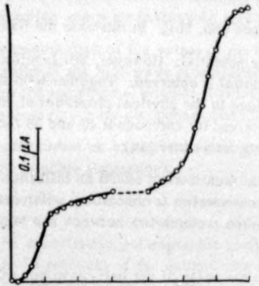


Fig. 2. Polarogram of compound 23 in acetate buffer solution.

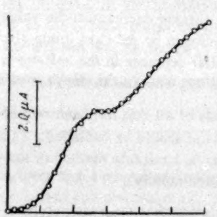
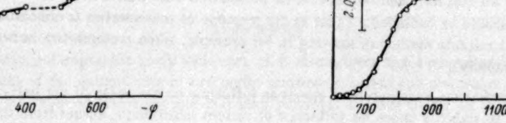


Fig. 3. Polarogram of compound 48 in acetate buffer solution.

The height of both waves corresponds to the electrode process with the participation of two electrons.

The pyridine derivative of the naphthoquinone (No.49), having a betaine structure, is also reduced in a peculiar manner with the appearance of two waves. The first of them probably corresponds to the reduction of the quinoid grouping, while the second is associated with the reduction of the pyridine ring (with the process being irreversible).

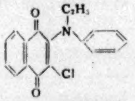
In analyzing the reasons for the strong influence exerted by the OH and NH_2 groups and its gradual reduction in the naphthoquinones with various substituents on the nitrogen it would seem that the latter could be explained as follows: 1) as due to the influence of the substituents (Y) on the state of the tautomeric equilibrium (a),



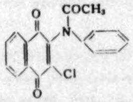
or 2) as due to the influence of the substituents on the intramolecular hydrogen bond (b).

In the first case the formation of an ortho-quinoid form should have led to a compound that is more easily reduced than the p-naphthoquinones. However, the magnitude of this difference was a total of 60-70 mV* [7], i. e. it proved to be considerably smaller than when substituents were present in some of the compounds (Table 1). In addition, the investigations of Fieser on the tautomerism of amino- and hydroxynaphthoquinones revealed that the total amount of the ortho-quinoid form in the equilibrium mixture is only about 0.2%, while for the aminonaphthoquinone (No. 10) the ortho-quinoid form is absent at all pH values of the solution.

To check on the presence of tautomerism in the naphthoquinone group we prepared several compounds in which the phenomenon of tautomerism is impossible. Such, for example, are the compounds



№ 24 ($\varphi_{1/2}$ = −152 mV)



№ 26 ($\varphi_{1/2}$ = −108 mV)

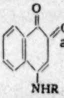
[compare with $\varphi_{1/2}$ = − 245 mV for 2-anilino-3-chloronaphthoquinone (No. 20)]. In this case the fixation of the para-quinoid structure should have led to a more negative half-wave potential. However, this is refuted experimentally, since a strong decrease in the value of the half-wave potential is observed. Together with this, replacement of hydrogen by the C_2H_5 group also leads to essential change in the physical properties of compounds [40, 41]. A similar decrease in the half-wave potential was also observed for compounds 43 and 38 (compare with Nos. 30 and 40), and also in the case of the corresponding bromo derivatives [40].

On the basis of all that has been said above, the postulation that tautomerism exerts an influence on the half-wave potential should be excluded. As far as the presence of tautomerism is concerned, polarography cannot serve in all cases as a reliable method of showing it, for example, when tautomerism between two tautomeric forms is established rapidly.

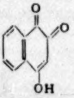
The postulation that the hydrogen bond exerts an influence on the value of the half-wave potential, as a result of a change in its stability under the influence of various substituents, ensues from the following facts. Compounds with an intramolecular hydrogen bond (Nos. 20, 30, 40, 42), when compared with compounds in which this bond is eliminated [ethylation (Nos. 24, 38, 43), acetylation (Nos. 26, 7), methylation (No. 5)], possess more negative values of the half-wave potentials, and for compounds Nos. 13, 14, 15, 19, 22, 23, 41, 42, etc. a change in the values of $\varphi_{1/2}$ is observed.

However, investigation of a possible hydrogen bond for the studied compounds reveals that in the case of a five-membered ring, with the distances between the nitrogen and oxygen atoms ranging from 2.87 to 3.1 A, it appears very weakly and can hardly exert substantial influence on the magnitude of the half-wave potential.

On the other hand, in the examination of some o-naphthoquinone derivatives with the same substituents (OH, NHR) [7, 8], where the formation of an intramolecular hydrogen bond is excluded,



and



it proves that the character of the influence of substituents is approximately the same for them as it is for the p-quinones. This suggests that the hydrogen bond is without substantial influence on the magnitude of $\varphi_{1/2}$ in the case of the arylaminonaphthoquinones and is not responsible for the sharp changes in the values of the half-wave potentials that exist for the derivatives with different substituents.

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* For o-naphthoquinone φ_0 = 555 mV, $\varphi_{1/2}$ = − 63 mV, and for 1,4-naphthoquinone (No. 1) $\varphi_{1/2}$ = −124 mV.

A comparison of the values of the half-wave potentials of compounds with different substituents in the case of naphthoquinones, and also in the case of o- and p-hydroxyazo compounds [42], reveals that the character of the substituents, as the result of their mutual influence in the molecule, is responsible for the substantial change in the values of the half-wave potentials. The reason for a change in the half-wave potential of a naphthoquinone with various substituents can be associated with a change in the electron density of the grouping being reduced as the result of a change in the mutual influence of the atoms and groups in the molecule.

Electron-donor groups (for example, OCH_3) shift the half-wave potential toward negative values, i. e. they increase the electron density at the quinoid grouping as the result of their effect being transmitted through the conjugated system of the benzene ring (see No. 19 and compare with No. 20; also compare Nos. 28 and 29 with No. 30). On the other hand, electron-acceptor groups (COOH, $SO_2 NH_2$, NO_2), due to their electron-unsaturation, cause a reduction in the electron density at the quinoid ring, which facilitates reduction and, as a consequence of this, causes the half-wave potential to shift toward the positive side (thus compare Nos. 13 and 15 with 11; Nos. 22 and 23 with 20; Nos. 36, 37, 31 and 32 with 30; and Nos. 41 and 42 with 40).

In connection with the COOH and $SO_2 NH_2$ groups attention is attracted to the fact that the sulfamido group lowers the half-wave potential of the naphthoquinone to a greater degree than does the carboxyl group (compare Nos. 13 and 15; 36 and 37; 41 and 42). This can be explained by the fact that the sulfamido group is a stronger electron-acceptor group than the carboxyl group. All of this is in agreement with the data on the dipole moments of sulfanilamide and p-aminobenzoic acid [43].

An examination of the values of the half-wave potentials of various naphthoquinone derivatives reveals that the value of the half-wave potential is affected not only by the character of the substituent, but also by its position in the molecule – whether it is found in the quinoid ring or in the ortho-, meta- or para-position in the phenyl radical (compare compounds Nos. 28 and 29; Nos. 31, 32 and 47; Nos. 33, 34 and 35).

In conclusion we express our deep gratitude to Prof. I. Ya. Postovsky for his interest in the work and for a number of valuable suggestions.

SUMMARY

1. A quantitative polarographic study was made of 49 derivatives of 1,4-naphthoquinone with substituents in the 2 and 3 positions of the quinoid ring in two buffer solutions (acetate and ammoniacal). It was shown that the naphthoquinones are reduced reversibly and that their potential depends on the pH of the solution.

2. The influence of various substituents on the magnitude of the half-wave potential was examined for both mono- and disubstituted naphthoquinones. Some additivity in the influence of the second group was shown in the case of the aminochloro- and aminoacetaminonaphthoquinone groups when compared with the aminonaphthoquinone.

3. A change in the magnitude of the half-wave potential of naphthoquinones as a function of various substituents can be explained as being due to a change in the electron density around the grouping being reduced, produced as the result of the mutual influence shown by the atoms and groups in the molecule.

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BUTYROLACTONE AND ITS DERIVATIVES

II. SOME REACTIONS OF THE ACYL DERIVATIVES OF BUTYROLACTONE

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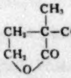
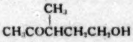
Some examples of the transformations of acyl derivatives of butyrolactone, possessing preparative significance, are described below. Examples of such reactions described up to now relate only to the carboxyl derivative of butyrolactone [1].

The reaction of methyl iodide with the sodio derivative of α-acetobutyrolactone readily yields α-methyl-α-acetylbutyrolactone (I) – a substance that is not obtained [2] in the condensation of the sodio derivative of α-methylacetoacetic ester with ethylene oxide.



(I)

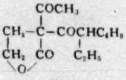


$CH_3CO\overset{CH_3}{\overset{|}{C}H}CH_2CH_2OH$

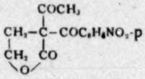
(II)

When boiled for a short time with dilute hydrochloric acid the methylated α-acetobutyrolactone suffers hydrolysis with the cleavage of carbon dioxide, similar to butyrolactone itself, yielding 3-methyl-1-pentano-4-one (II).

When a suspension of sodio-α-acetobutyrolactone in benzene is treated with the chloride of 2-ethylcaproic acid, taken as an example of a chloride of an acid of average molecular weight, the corresponding diacyl derivative (III) is formed, and with p-nitrobenzoyl chloride the corresponding diacyl derivative (IV) is formed.



(III)

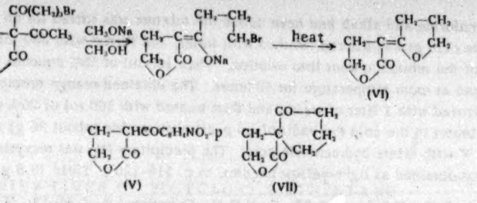


(IV)

In contrast to the analogs of the acetoacetic ester series, it is not the acetyl group that is cleaved in the alcoholysis of (III), but instead it is the ethylcaproic acid part with regeneration of the acetobutyrolactone. It proves impossible to obtain a higher acyl derivative of butyrolactone in this manner. At the same time the ammonolysis of (IV) leads to the formation of p-nitrobenzoylbutyrolactone (V), but in small yield.

The alcoholysis of the product of the acylation of α-acetobutyrolactone with γ-bromobutyryl chloride proceeds in a very peculiar manner. Here the dibutyrolactone (VI) is formed, first described by Fittig [3].

Evidently, the reaction proceeds in accord with the scheme,


(VI) (V) (VII)

and represents a rare case of the alkylation of a β-dicarbonyl compound at the oxygen atom, since the usual alkylation at the carbon atom should have led to the formation of the spiroketolactone (VII).

Hunsdiecker described [4] analogous cyclizations of ω-bromoacylacetic esters; however, in all cases reaction led to the formation of isocyclic compounds.

EXPERIMENTAL

Methylation of α-Acetobutyrolactone. To a suspension of 2.3 g of sodium in 60 ml of benzene was added in one portion 12.8 g of acetobutyrolactone* and 10 drops of methanol. The mixture was shaken at periodic intervals during the next 4 hours, and toward the end was heated until all of the sodium had dissolved. The obtained suspension was treated with 17 g of methyl iodide and the mixture was boiled until the reaction was no longer alkaline (about 3 hours). Then a small amount of water was added, the benzene layer was separated, and then it was dried over magnesium sulfate. The residue after distilling off the benzene was vacuum-distilled. The fraction with b.p. 112-118° at 12 mm weighed 10.5 g (75%). For analysis the substance was distilled twice in vacuo. The oily liquid had a nutty odor.

B.p. 125-126° at 18 mm, d_4^{20} 1.1464, n_D^{20} 1.4561, MR_D 33.70; calc. 33.98.

Found %: C 59.12; H 6.90; equiv. 136.9. $C_7H_{10}O_3$. Calculated %: C 59.16; H 7.11; equiv. 142.1.

The semicarbazone was obtained from 2 g of the ketolactone, 2 g of semicarbazide hydrochloride and 2 g of potassium acetate in 20 ml of water. Fine needles from alcohol with m.p. 190°.

Found %: N 21.24. $C_8H_{13}O_3N_3$. Calculated %: N 21.10.

Ketonic Cleavage. A mixture of 2.5 g of the ketolactone (I) and 15 ml of 5% hydrochloric acid was boiled for 30 minutes. The oil went into solution with the evolution of carbon dioxide. After cooling the solution was saturated with potash and the resulting oily layer separated. The substance (II), weighing 2 g (98%), was vacuum-distilled twice. Quite mobile liquid with b.p. 89° at 9 mm.

d_4^{20} 0.9811, n_D^{20} 1.4405, MR_D 31.21; calc. 31.44.

Found %: C 62.14; H 10.23. $C_6H_{12}O_2$. Calculated %: C 62.00; H 10.42.

Acylation of α-Acetobutyrolactone. a) To a suspension of the sodio derivative, prepared, as described above, from 6 g of sodium and 32 g of α-acetobutyrolactone in 200 ml of benzene, was added 40.5 g of 2-ethylcaproyl chloride.** The mixture was boiled for 1.5 hours (until the reaction was no longer alkaline). The benzene solution was filtered from salt, washed with water, and dried over magnesium sulfate. The residue after distilling off the benzene was vacuum-distilled. The substance (III) was a thick yellowish liquid with b.p. 155-156° at 1 mm, n_D^{20} 1.4737.

Found %: C 66.52; H 9.03. $C_{14}H_{22}O_4$. Calculated %: C 66.12; H 8.72.

Alcoholysis of (III) with sodium methylate in benzene-alcohol solution led to the formation of α-acetobutyrolactone and methyl α-ethylcaproate (88%).

b) A suspension of 70 g of α-acetobutyrolactone in 80 ml of water was acylated by the Schotten-Baumann method with 93 g of p-nitrobenzoyl chloride in acetone (125 ml) solution, employing 20 g of sodium hydroxide in 80 ml of water. During reaction the alkalinity was kept at a pH of 8-9 and the temperature was kept at 10-15°.

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* The compound, obtained according to [5], had b.p. 135-137° at 20 mm and n_D^{20} 1.4590.

** B.p. 60-62° at 10 mm, obtained from 2-ethylcaproic acid and thionyl chloride. 2-Ethylcaproic acid was obtained from 2-ethylhexanol in known manner [6].

When all of the chloride and alkali had been added the mixture was stirred for an additional 3 hours. The obtained precipitate (110 g) was filtered, washed with water, and stirred with 600 ml of methanol. A substantial portion of the substance went into solution. Then 100 ml of 15% aqueous ammonia was added, and the mixture was stirred at room temperature for 12 hours. The obtained orange precipitate was filtered, washed with methanol, stirred with 1 liter of water, and then treated with 100 ml of 25% sodium hydroxide at 0°. After stirring for 30 minutes in the cold the undissolved p-nitrobenzamide (about 36 g) was filtered, and the filtrate was acidified at 0° with dilute hydrochloric acid. The precipitate (V) was recrystallized twice from alcohol. The substance was obtained as light-yellow needles, m.p. 119-120°. Yield 13.8 g (12%).

Found %: C 56.43; H 3.76; N 5.97. $C_{11}H_9O_5N$. Calculated %: C 56.17; H 3.85; N 5.96.

c) To a suspension of the sodio derivative, prepared from 25.6 g of α-acetobutyrolactone and 4.6 g of sodium in 100 ml of benzene, was added in small portions 36 g of γ-bromobutyryl chloride, * and the mixture was heated at weak boil for 1 hour. The cooled mixture was treated with 70 ml of water, the benzene layer was separated, and the water layer was extracted twice with benzene. The benzene solution was dried over magnesium sulfate and the solvent was removed by distillation. The volatile impurities were removed from the residue by heating at 0.5 mm and 150°; then it was stirred with a solution of 3 g of sodium in 50 ml of methanol. The solution was boiled for 2 hours, the solvent removed by distillation, and the residue diluted with two volumes of water. The obtained oil was extracted with benzene. After drying and removal of the solvent by distillation the residue was vacuum-distilled. The fraction with b.p. 120-150° at 0.5 mm was collected, and partially crystallized on cooling. The separated mother liquor was again distilled, collecting the fraction with b.p. 120-130° at 0.5 mm, which also partially crystallized. The distillation and crystallization were repeated once more. The total yield of colorless crystalline substance (VI) was 5 g (16%). Lustrous leaflets with m.p. 86-87° (from water).

Found %: C 62.46; H 6.70. $C_8H_{10}O_3$. Calculated %: C 62.35; H 6.56.

SUMMARY

Some examples of the alkylation and acylation of α-acetobutyrolactone were described, leading to the formation of some new butyrolactone derivatives.

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* The compound described by Child and Pyman [7], i.e. with b.p. 94-95° at 30 mm.

** Original Russian pagination. See C.B. Translation.

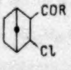
DERIVATIVES OF BICYCLO-1,2,3-HEPTANE

II. DERIVATIVES OF 2-ACYL-3-AMINOBICYCLO-(1,2,2)-HEPTANE

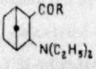
N. K. Kochetkov, A. Ya. Khorlin and O. S. Chizhov

In the previous communication [1] and in earlier papers [2, 3] we have established the high reactivity of 2-acyl-3-chlorobicyclo-(1,2,3)-heptanes (I), and having reacted these compounds with sodium alcoholates and phenolates, salts of organic acids and metallic derivatives of β-dicarboxylic compounds, we have demonstrated the possibility of using them in the synthesis of various derivatives of bicyclo-(1,2,2)-heptane.

In the present paper we report on the synthesis and reactions of 2-acyl-3-diethylaminobicyclo-(1,2,2)-heptanes (II, R = CH_3, C_2H_5, C_3H_7, C_6H_5).



(I)



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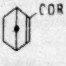
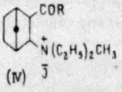


(III)



(IV)

These compounds are of interest primarily because, being β-aminoketones they should possess a mobile amino group, as is well known in the case of Mannich bases. In addition they also deserve a more detailed investigation on account of their physiological activity as there have recently appeared reports indicating that amines of bicycloheptane possess valuable pharmacological properties [4].

The starting materials for the synthesis of the compounds in question were the corresponding 2-acyl-3-chlorobicyclo-(1,2,2)-heptanes (I) which can be easily obtained by condensation of cyclopentadiene with β-chlorovinylketones, a reaction which has been developed previously in this laboratory [5]. Attempts to substitute the chlorine atom in (I) by the diethylamino group in alcoholic or aqueous solution did not give satisfactory results since the reaction proceeds very slowly and is never complete as a result of which there is formed a complex mixture of various compounds together with a considerable quantity of resinous products. The reaction was found to proceed best on heating the chloroketones (I) in an excess of diethylamine. Under these conditions substitution of the chlorine by the diethylamino group proceeds smoothly and the required aminoketones (II) are obtained in 40-70% yields. It is interesting to note that while 2-acetyl-3-chlorobicyclo-(1,2,2)-heptane is transformed under these conditions into the aminoketone to an extent of 70% after only 3 hours heating, a much longer heating period (6-15 hours) is necessary in the latter cases in order to obtain a satisfactory result, and it is found that aliphatic derivatives (I, R = C_2H_5 or C_3H_7) react less readily than does 2-benzoyl-3-chlorobicyclo-(1,2,2)-heptane (I, R = C_6H_5).

In all cases we found that the formation of the aminoketones (II) was accompanied by the formation of a considerable quantity of a neutral fraction (10-20%) which in the case of the methyl homolog (I, R = CH_3) was found to be pure 2-acetyl-bicyclo-(1,2,2)-heptene-2 (III, R = CH_3), and was identical with the one described previously [2]. In all the other cases the neutral fraction was found to be a mixture of the unsaturated ketone (III) and the original chloroketone (I) and was not examined in greater detail.

The aminoketones (II) thus prepared are colorless or yellowish viscous liquids with boiling points which are considerably higher than the boiling point of the original chloroketone, a fact which is of essential importance in their isolation. When kept at low temperatures they remain unchanged for long periods. Like the more familiar β-aminoketones, they easily form hydrochlorides, picrates and alkiodides. Of these derivatives the methiodides (IV) present the greatest interest; they are obtained in practically quantitative yields on simply mixing the aminoketones with methyl iodide.

The compounds obtained resemble, formally, analogs of Mannich bases. The particular feature of our compounds is the presence of a radical in the β-position to the carboxylic group, a structure which on account of the very method of their preparation cannot be found in the usual Mannich bases. In this connection it was of interest to elucidate the problem of the lability of the dialkylamino group in the aminoketones (II) and to determine what effect the presence of this radical in the beta position and, above all, the rigid bicycloheptane structure have on the mobility of the amino group. For this purpose we have investigated the behavior of 2-acetyl-3-diethylaminobicyclo-(1,2,2)-heptane (II, R = CH_3) and of its methiodide (IV, R = CH_3) in the Mannich-Robinson reaction. It was found that both these compounds condense easily with the malonic ester under the usual conditions in the presence of sodium alcoholate giving rise, in both bases, to the formation in 40-55% yield of 2-acetylbicyclo-(1,2,2)-heptyl-(3)-malonic ester which was found to be identical with the one synthesized previously starting with 2-acetyl-3-chlorobicyclo-(1,2,2)-heptane (I).

These results show that derivatives of 2-acyl-3-aminobicyclo-(1,2,2)-heptane behave in the same manner as do the usual Mannich bases and that they may be used successfully in similar reactions. It is possible that in certain specific respects these derivatives may prove more useful than the corresponding chloroketones (I). In addition, the results obtained by us show that the carbon atom skeleton of bicycloheptane does not undergo any rearrangement when the chloroketones (I) interact with amines; this is in agreement with results obtained in previous investigations [1-3]. Furthermore, substitution in the amino group in the aminoketones (II) also proceeds normally and without any structural rearrangements.

EXPERIMENTAL

2-Acetyl-3-diethylaminobicyclo-(1,2,2)-heptane. A mixture of 35.5 g of 2-acetyl-3-chlorobicyclo-(1,2,2)-heptane and 150 ml of diethylamine was refluxed gently for three hours with constant stirring. The diethylamine hydrochloride which separated was filtered off, exess diethylamine was removed from the filtrate and the residue was dissolved in 5 N hydrochloric acid added in an amount necessary to obtain acid reaction to Congo red. The insoluble neutral oil which separated was extracted with ether. The acid aqueous solution was made alkaline with excess of 20% caustic soda, the oily amino ketone formed was separated, the aqueous layer extracted with ether, the extracts were added to the bulk of the substance and dried over potassium hydroxide. After removing the ether the residue was distilled in vacuo. Yield of 2-acetyl-3-diethylaminobicyclo-(1,2,2)-heptane, 30.6 g (71.2%).

B. p. 104-106° at 7 mm, n_D^{20} 1.4853, d_4^{20} 0.9635.

Found %: C 74.30, 74.13; H 10.84, 10.84. $C_{13}H_{23}ON$. Calculated %: C 74.59; H 11.08.

The colorless oil is miscible with organic solvents, gradually assumes a yellow color on storage and may be kept in the cold for long periods without change.

From the neutral fraction which separated on treatment following the removal of ether and distillation in vacuo, there was obtained 5.0 g (17.8%) of 2-acetylbicyclo-(1,2,2)-heptene-2, b. p. 65-69° at 5 mm, n_D^{20} 1.4970. Literature [2], b.p. 54-56° at 2 mm, n_D^{20} 1.4972.

The picrate was formed in and recrystallized from methanol. Yellow needles, b. p. 163-164°.

Found %: N 12.93, 12.97. $C_{19}H_{26}O_8N_4$. Calculated %: N 12.85.

The hydrochloride was obtained by saturating a solution of 2-acetyl-3-diethylaminobicyclo-(1,2,2)-heptane in methanol with dry hydrogen chloride. The heavy viscous oil which was obtained after removal of methanol gradually crystallized. After recrystallization from methanol the substance was obtained in the form of colorless crystals melting at 131-132°.

Found %: Cl 14.35; 14.43. $C_{13}H_{24}ONCl$. Calculated %: Cl 14.43.

The methiodide was formed from 6 g of 2-acetyl-3-diethylaminobicyclo-(1,2,2)-heptane and 10 ml of methyl iodide. On mixing the reagents there was evolution of heat and the mixture boiled spontaneously. It was allowed to stand overnight, the crystals which separated were filtered off, washed with dry ether and reprecipitated from acetone with dry ether. Yield, 8.5 g (84%). Colorless needles, m.p. 174°.

Found %: I 36.50, 36.52. $C_{14}H_{26}ONI$. Calculated %: I 36.15.

The substance is soluble in water, alcohol, and insoluble in ether.

The ethiodide was formed after heating 2-acetyl-3-diethylaminobicyclo-(1,2,2)-heptane with 10 ml of ethyl iodide on a water bath for 10 hours. After treatment similar to the one followed in the case of the methiodide there was obtained 4.2 g (60%) of the ethiodide in the form of colorless needles melting at 135-136°.

Found %: I 34.89, 34.96. $C_{15}H_{28}ONI$. Calculated %: I 34.73.

2-Propionyl-3-diethylaminobicyclo-(1,2,2)-heptane was obtained by a method similar to the one above, namely, by heating 15.0 g of 2-propionyl-3-chlorobicyclo-(1,2,2)-heptane and 75 ml of diethylamine for 15 hours. Yield, 11.2 g (62%).

B. p. 117-119° at 5 mm, n_D^{20} 1.4812; d_4^{20} 0.9441.

Found %: C 75.17, 74.93; H 10.92, 10.73. $C_{14}H_{25}ON$. Calculated %: C 75.28; H 11.28.

The picrate was formed in methanol as yellow glistening flakes, m.p. 150-151° (from methanol).

Found %: N 12.92, 12.86. $C_{20}H_{28}O_8N_4$. Calculated %: 12.78.

The methiodide was obtained and purified in a manner similar to the one above. Colorless crystals, m.p. 143-144°.

Found %: I 35.00, 35.05. $C_{25}H_{28}ONI$. Calculated %: 34.73.

2-Butyryl-3-diethylaminobicyclo-(1,2,2)-heptane was obtained in an analogous manner by heating 33.5 g of 2-butyryl-3-chlorobicyclo-(1,2,2)-heptane with 125 ml of diethylamine for 15 hours. Yield, 17.1 g (43.5%).

B. p. 120-122° at 5 mm, n_D^{20} 1.4808, d_4^{20} 0.9172.

Found %: C 76.21, 76.29; H 11.54, 11.40. $C_{15}H_{27}ON$. Calculated %: C 75.87; H 11.47.

The methiodide was obtained and purified as above. Colorless crystals, m.p. 136-137°.

Found %: I 33.61, 33.47. $C_{16}H_{30}ONI$. Calculated %: I 33.45.

2-Benzoyl-3-diethylaminobicyclo-(1,2,2)-heptane. 5.0 g of 2-benzoyl-3-chlorobicyclo-(1,2,2)-heptane and 25 ml of diethylamine was refluxed for 6 hours. Excess diethylamine was distilled off and the residue dissolved in excess of 20% hydrochloric acid. After extracting from the acid solution a small quantity of neutral impurities, the hydrochloride of 2-benzoyl-3-diethylaminobicyclo-(1,2,2)-heptane, sparingly soluble in water, separated gradually from the aqueous layer. It was filtered off, dried in vacuo and recrystallized from acetone. Yield 4.1 g (63%) in the form of colorless crystals melting at 179-180°.

Found %: Cl 11.40, 11.38. $C_{18}H_{26}ONCl$. Calculated %: Cl 11.52.

The substance is soluble in acetone, sparingly soluble in water and insoluble in ether. On treatment with alkali there precipitates the oily base which does not crystallize and is difficult to purify.

The picrate was formed in methanol as fine yellow crystals melting at 177-178°.

Condensation of 2-acetyl-3-diethylaminobicyclo-(1,2,2)-heptane with diethyl malonate. A mixture of 10.5 g 2-acetyl-3-diethylaminobicyclo-(1,2,2)-heptane and 8 g of diethyl malonate was heated in 25 ml of ethyl alcohol, in the presence of 0.15 g of sodium, for 10 hours at 60-65°. Excess alcohol was removed, the residue poured into 25 ml of water and the solution acidified with 1 ml of concentrated sulfuric acid. The oil which separated was extracted with ether, the extracts were dried over sodium sulfate, the ether was removed and the residue distilled in vacuo. Yield of 2-acetylbicyclo-(1,2,2)-heptyl-(3)-malonic ester, 6 g (40%), b.p. 164-166° at 3 mm, n_D^{20} 1.4736. Literature [1], b.p. 150-151° at 1.5 mm, n_D^{20} 1.4730.

2,4-Dinitrophenylhydrazone of 2-acetylbicyclo-(1,2,2)-heptyl-(3)-malonic ester was obtained as described previously [1], m.p. 123°. Mixture with an authentic sample of the substance did not depress the melting point. Literature [1], m.p. 124-125°.

Condensation of 2-acetyl-3-diethylaminobicyclo-(1,2,2)-heptane methiodide with malonic ester. To a solution of the sodium derivative of diethyl malonate, prepared by the usual method from 12 g of diethyl malonate and 1.2 g of sodium in 60 ml of alcohol, was added 17 g of methyl iodide and the mixture was heated on a water bath for 15 hours. After the treatment described in the foregoing example there was obtained, on distillation, 8 g (55%) of 2-acetylbicyclo-(1,2,2)-heptyl-(3)-malonic ester, b.p. 170-172° at 5 mm, n_D^{20} 1.4731.

The 2,4-dinitrophenylhydrazone was obtained as described, m.p. 120-123°. Mixture with an authentic sample as well as with a sample of the substance described in the foregoing example, did not depress the melting point.

SUMMARY

1. By reacting 2-acyl-3-chlorobicyclo-(1,2,2)-heptanes with diethylamine the authors have prepared the corresponding 2-acyl-3-diethylaminobicyclo-(1,2,2)-heptanes (in 40-70% yields) which, in turn, give the hydrochlorides, methiodides and picrates, as do the usual β-aminoketones.

2. 2-Acyl-3-ethylaminobicyclo-(1,2,2)-heptanes and their methiodides enter into Mannich-Robinson condensation reactions (e.g. with the malonic ester) giving rise to the formation of the normal products of such reactions.

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INDOLE DERIVATIVES

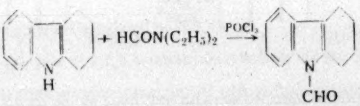
IV. FORMYLATION OF DERIVATIVES OF 1,2,3,4-TETRAHYDROCARBAZOLE

N. F. Kucherova, V. P. Evdakov and N. K. Kochetkov

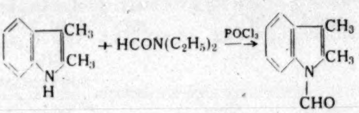
In the course of the investigation of the physiological activity of certain derivatives of 1,2,3,4-tetrahydrocarbazole it was necessary to prepare aldehydes of this compound and of its derivatives which would contain the aldehydic group in the aromatic nucleus; aldehydes of this type have until now been unknown. The most suitable method of synthesizing compounds of this type appeared to be by formylation of 1,2,3,4-tetrahydrocarbazole and of its N-substituted derivatives. The investigation of this synthesis is the subject of the present paper.

The introduction of the formyl group by means of N-substituted formamides in the presence of phosphorus oxychloride has in recent years found application in the synthesis of aldehyde derivatives of pyrrole [1], indole [2], thiophene [3] etc. It has been reported that N-alkylcarbazole under these conditions gives N-alkylcarbazole-6-aldehyde [4].

Our investigation started with the formylation of 1,2,3,4-tetrahydrocarbazole itself. When the reaction was carried out under the usual conditions, i. e. by the interaction of tetrahydrocarbazole with excess diethylformamide in the presence of phosphorus oxychloride there was obtained, in good yield, a stable compound whose composition corresponded with a mono-formyl derivative of 1,2,3,4-tetrahydrocarbazole. The compound obtained did not manifest the properties of an aldehyde (it gave neither the requisite derivatives nor the reactions for the carbonyl group) and on hydrolysis either in an alkaline or acid medium it easily decomposed with the formation of the original tetrahydrocarbazole and formic acid. This indicates that the substance obtained was a N-formyl derivative of 1,2,3,4-tetrahydrocarbazole the formation of which may be expressed by the equation



Thus, formylation of tetrahydrocarbazole proceeds differently from the formylation of indole which gives rise to indole-3-aldehyde [2]. Since 1,2,3,4-tetrahydrocarbazole is, in fact, a 2,3-disubstituted indole, the result obtained may be regarded as characteristic of the formylation of 2,3-disubstituted derivatives of indole. In fact, it was found that formylation of 2,3-dimethyl-indole also takes place at the nitrogen atom with the formation of 1-formyl-2,3-dimethylindole.

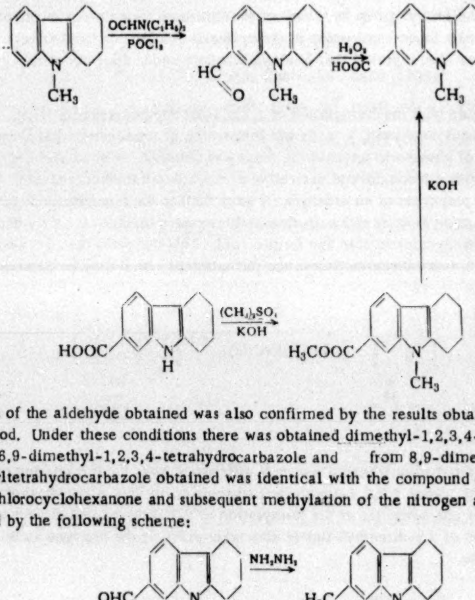


The structure of this compound was proved by hydrolysis which leads to the regeneration of the original 2,4-dimethylindole.

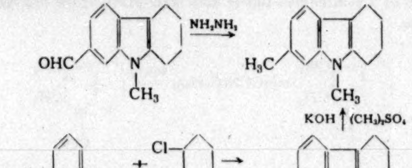
Attempts to introduce a second formyl group into 1,2,3,4-tetrahydrocarbazole by using excess of reagents or by carrying out the reaction under more drastic conditions, were unsuccessful. This was confirmed by the fact that in an attempted formylation of 9-formyl-1,2,3,4-tetrahydrocarbazole described above the latter did not at all enter into reaction and could be recovered quantitatively.

Subsequently we turned to the formylation of 9-methyl-1,2,3,4-tetrahydrocarbazole. In this case there was obtained, in 34% yield, a single compound which possessed the properties of an aldehyde: it gave rise to the formation of derivatives through the carbonyl group and also gave the usual qualitative reactions. The compound obtained was investigated in detail with the object of determining the position of the aldehyde group in the aromatic nucleus. It might be expected that formylation of 1,2,3,4-tetrahydrocarbazole would take place at position 6, as is the case with N-alkylcarbazoles, or at position 8; quite unexpectedly, however, it was found that the reaction took a different course.

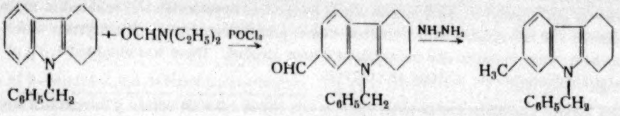
On oxidation of this aldehyde with hydrogen peroxide there was obtained an acid melting at 274-276° (its methyl ester melted at 126-128°). Both the acid and its ester gave a sharp depression of the melting point when mixed with 6-carboxy-9-methyl-1,2,3,4-tetrahydrocarbazole or with a corresponding ester, which have been prepared by us. However, they were found to be identical, respectively, with 7-carboxy-9-methyl-1,2,3,4-tetrahydrocarbazole and its ester. These results show that formylation of 9-methyl-1,2,3,4-tetrahydrocarbazole leads to the formation of 7-formyl-9-methyl-1,2,3,4-tetrahydrocarbazole and the reactions described may be represented by the following scheme:



The structure of the aldehyde obtained was also confirmed by the results obtained by its reduction by the Wolff-Kishner method. Under these conditions there was obtained dimethyl-1,2,3,4-tetrahydrocarbazole which differed both from 6,9-dimethyl-1,2,3,4-tetrahydrocarbazole and from 8,9-dimethyl-1,2,3,4-tetrahydrocarbazole. The dimethyltetrahydrocarbazole obtained was identical with the compound obtained by condensation of m-toluidine with chlorocyclohexanone and subsequent methylation of the nitrogen atom. These transformations may be represented by the following scheme:



Next we have carried the formylation of 9-benzyl-1,2,3,4-tetrahydrocarbazole which also gave a single compound possessing the properties of an aldehyde and which was found to be 7-formyl-9-benzyl-1,2,3,4-tetrahydrocarbazole. On reducing this by the Wolff-Kishner method there was obtained 7-methyl-9-benzyl-1,2,3,4-tetrahydrocarbazole.



The above investigations show that formylation by means of N-substituted formamides may be used with success in the synthesis of aldehydes of N-substituted 1,2,3,4-tetrahydrocarbazoles the preparation of which by other methods presents considerable difficulty. Of particular interest in this case is the formation of 7-substituted aldehydes. The observed substitution in position 7 of the tetrahydrocarbazole nucleus (which corresponds to substitution in position 6 in the case of the indole ring) is of considerable interest and deserves more detailed investigation.

EXPERIMENTAL

Formylation of 1,2,3,4-tetrahydrocarbazole. To 6 g of 1,2,3,4-tetrahydrocarbazole and 30 g of diethyl formamide was added 6 g of phosphorus oxychloride, the mixture was heated on a water bath for eight hours, cooled, and neutralized with 30% aqueous solution of potassium acetate. Excess diethyl formamide was removed by steam-distillation, the reaction mass was cooled and extracted with ether (three 50 ml portions), the extracts washed several times with water and dried over sodium sulfate. After removing the ether the residue was distilled in vacuo and the fraction boiling at 175-185° at 4 mm was collected; the latter crystallized in the receiver. After recrystallization from a small amount of ether the substance melted at 64.5-65.5°. Yield, 4.5 g (65%).

Found %: C 78.45, 78.19; H 6.52, 6.54; N 7.03, 7.03. $C_{13}H_{13}ON$. Calculated %: C 78.38; H 6.57; N 7.03.

The substance is in the form of colorless crystals which are soluble in benzene, ethyl acetate, ether and acetone and difficultly soluble in alcohol. When the above reaction is carried out in the presence of an amount of phosphorus oxychloride 10-12 times in excess of that used above, the result of the reaction is the same.

Hydrolysis of 9-formyl-1,2,3,4-tetrahydrocarbazole. Two g of 9-formyl-1,2,3,4-tetrahydrocarbazole was heated for two hours with 20 ml of 7% alcoholic potassium hydroxide. The reaction mixture was cooled and 30 ml of water was added. The mixture was extracted with ether, the extracts dried over sodium sulfate. The ether was removed and after recrystallization from alcohol there was obtained 1,2,3,4-tetrahydrocarbazole. Yield, 1.3 g (71%), m.p. 112-114°.

Found %: N 8.10, 8.08. $C_{12}H_{13}N$. Calculated %: N 8.17.

Mixture with an authentic sample of 1,2,3,4-tetrahydrocarbazole did not depress the melting point.

The aqueous-alcoholic alkaline solution was acidified with sulfuric acid and steam-distilled. Formic acid was detected in the distillate by qualitative tests (discoloration of potassium permanganate; orange coloration with resorcin and sulfuric acid).

Hydrolysis of 9-formyl-1,2,3,4-tetrahydrocarbazole with an alcoholic solution of hydrogen chloride gave a similar result.

Formylation of 2,3-dimethylindole. A mixture of 2 g of 2,3,-dimethylindole, 11 g of diethyl formamide and 2 g of phosphorus oxychloride was heated on a water bath for 6 hours. After the usual treatment there was obtained 1-formyl-2,3-dimethylindole. Yield 0.7 g (30.4%), m.p. 84-86°.

Found %: C 76.04, 76.19; H 6.52, 6.54; N 8.24, 8.08. $C_{11}H_{11}ON$. Calculated %: C 76.28; H 6.47; N 8.08.

Colorless crystals, soluble in ether, alcohol, benzene and acetone.

Hydrolysis of 1-formyl-2,3-dimethylindole. 1 g of 1-formyl-2,3-dimethylindole and 20 ml of 2% alcoholic alkali was heated for 1½ hours. The alcohol was removed in vacuo, the reaction mixture was cooled, neutralized and extracted with ether. The extracts were dried, the ether removed and the residue recrystallized from 50% aqueous alcohol. There was obtained 0.7 g (70.1%) of 2,3-dimethylindole, m.p. 98-100°. Mixture of the substance with a sample of 2,3-dimethylindole did not depress the melting point.

Formylation of 9-methyl-1,2,3,4-tetrahydrocarbazole. A mixture of 4 g of 9-methyl-1,2,3,4-tetrahydrocarbazole, 23 g of diethyl formamide and 4 g of phosphorus oxychloride was reacted in the manner indicated above, cooled and neutralized with a 30% solution of potassium acetate. The crystals which separated on cooling in an ice-bath were removed and recrystallized from alcohol. There was obtained 1.3 g of 7-formyl-9-methyl-1,2,3,4-tetrahydrocarbazole melting at 113-114°.

The filtrate was diluted with water (20 ml) and extracted with ether. The extracts were washed several times with water, dried over sodium sulfate, the ether removed and the residue recrystallized from alcohol yielding another 0.3 g of the 7-formyl derivative. Total yield 1.6 g (34%).

Found %: C 78.67, 78.64; H 7.26, 7.26; N 6.40, 6.64. $C_{14}H_{15}ON$. Calculated %: C 78.83; H 7.09; N 6.56.

Colorless crystals, soluble in benzene, acetone, ether and ethyl acetate and sparingly soluble in alcohol.

The phenylhydrazone was formed by heating 0.3 g of the compound obtained with 0.18 g of phenylhydrazine on a water bath for 30 minutes, cooling and recrystallizing the crystalline mass from benzene. Yield of 7-formyl-9-methyl-1,2,3,4-tetrahydrocarbazole phenylhydrazone, 0.33 g (75%), m. p. 163-165° (decomp.)

Found %: N 13.65, 13.95. $C_{20}H_{21}N_3$. Calculated %: N 13.83.

Oxidation of 7-formyl-9-methyl-1,2,3,4-tetrahydrocarbazole. A solution of 2 g of 7-formyl-9-methyl-1,2,3,4-tetrahydrocarbazole in 100 ml of 2% alcoholic potassium hydroxide was heated to 60°. To this was added over 1 hour, with stirring, 50 ml of 26% hydrogen peroxide after which the solution was heated for another hour. The alcohol was then removed, the solution cooled and extracted with ether. The aqueous layer was acidified with hydrochloric acid and extracted with ether (3 x 60 ml). The extracts were washed with water, dried over sodium sulfate, the ether was removed and the residue recrystallized from glacial acetic acid (in the presence of charcoal). Yield of 7-carboxy-9-methyl-1,2,3,4-tetrahydrocarbazole, 0.9 g (47.6%) m.p. 274-276° (decomp.).

Found %: C 73.40, 73.36 H 6.60, 6.61; N 6.26, 6.23. $C_{14}H_{15}O_2N$. Calculated %: C 73.34; H 6.58; N 6.11.

The crystals are sparingly soluble in benzene and ether, and more soluble in acetone and alcohol.

A mixture of the substance with an authentic sample of 6-carboxy-9-methyl-1,2,3,4-tetrahydrocarbazole (for preparation see below, m.p. 288-289°) melts at a strongly depressed temperature (220-260°). Mixture with 7-carboxy-9-methyl-1,2,3,4-tetrahydrocarbazole, obtained by a different method (see below), did not depress the melting point.

0.4 g of the acid and 10 ml of 15% solution of hydrogen chloride in anhydrous methanol was heated for three hours. After removal of half the alcohol the reaction mixture was cooled and the precipitate which formed was recrystallized from alcohol yielding 0.2 g (47%) of 7-carbmethoxy-9-methyl-1,2,3,4-tetrahydrocarbazole, m.p. 126-128°. The colorless needles are soluble in ether, benzene and acetone.

Mixture of the substance with a sample of 6-carbmethoxy-9-methyl-1,2,3,4-tetrahydrocarbazole (for preparation see below, m.p. 155-157°) melted with strong depression (103-122°). Mixture with 7-carbmethoxy-9-methyl-1,2,3,4-tetrahydrocarbazole, obtained by a different method (see below) did not depress the melting point.

Reduction of 7-formyl-9-methyl-1,2,3,4-tetrahydrocarbazole. 2 g of 7-formyl-9-methyl-1,2,3,4-tetrahydrocarbazole, 5 ml of hydrazine hydrate, 30 g of potassium hydroxide and 20 ml of diethylene glycol was heated during one hour at 100-110°, the water and excess hydrazine hydrate were removed, the residual mixture was refluxed for 3 hours, cooled, diluted with water and extracted with ether. The ether extracts were washed with water, dried over sodium sulfate, the ether was removed and the residue recrystallized from alcohol. Yield of 7,9-dimethyl-1,2,3,4-tetrahydrocarbazole, 1.5 g (80%), m.p. 102-104°.

Found %: C 84.51, 84.32; H 8.85, 8.69; N 7.06, 6.99. $C_{14}H_{17}N$. Calculated %: C 84.37; H 8.59; N 7.02.

Colorless crystals soluble in ether, acetone, benzene and ethyl acetate; and less soluble in alcohol.

Mixture of the substance with a sample of 6,9-dimethyl-1,2,3,4-tetrahydrocarbazole [5] (m.p. 90°) gave a strong depression of the melting point (74-82°). Mixture with 8,9-dimethyl-1,2,3,4-tetrahydrocarbazole (for preparation see below, m.p. 147-149°) also depressed the melting point (85-91°). Mixture with a sample of 7,9-dimethyl-1,2,3,4-tetrahydrocarbazole, obtained by a different method (see below), did not depress the melting point.

Formylation of 9-benzyl-1,2,3,4-tetrahydrocarbazole. 5 g of 9-benzyl-1,2,3,4-tetrahydrocarbazole [6], 21 g of diethyl formamide and 5 g of phosphorus trioxide was reacted as described above. Yield of 7-formyl-9-benzyl-1,2,3,4-tetrahydrocarbazole, 2.0 g (36%), m.p. 89-91° (from a mixture of alcohol and ethyl acetate).

Found %: N 4.86, 4.77. $C_{20}H_{19}ON$. Calculated %: N 4.83.

The yellowish crystals are soluble in ether, benzene and acetone and difficultly soluble in alcohol.

The azine. 1 g of the substance and 3 g of hydrazine hydrate was heated on a water bath for three hours. The mixture was cooled, 5 ml of water was added, the mixture filtered, washed with water and triturated with acetone. After filtration and recrystallization from pyridine there was obtained 7-formyl-9-benzyl-1,2,3,4-tetrahydrocarbazole azine, yield 0.7 g (77%), m.p. 265-267°.

Found %: N 9.83; 9.73. $C_{40}H_{38}N_4$. Calculated %: N 9.74.

The phenylhydrazone. 0.5 g of the substance and 0.23 g of phenylhydrazine was heated on a water-bath for 30 minutes. After cooling, the crystalline mass was recrystallized from a mixture of alcohol and acetone (1 : 1) followed by recrystallization from benzene. Yield of 7-formyl-9-benzyl-1,2,3,4-tetrahydrocarbazole, 0.55 g (84%). M.p. 153-155°) (decomp.).

Found %: N 10.81, 10.95. $C_{26}H_{25}N_3$. Calculated %: N 11.07.

Reduction of 7-formyl-9-benzyl-1,2,3,4-tetrahydrocarbazole. 1 g of 7-formyl-9-benzyl-1,2,3,4-tetrahydrocarbazole was reduced by the Wolff-Kishner method as described above. Yield of 7-methyl-benzyl-1,2,3,4-tetrahydrocarbazole, 0.7 g (77%), m.p. 66-68°, from alcohol.

Found %: N 5.40; 5.20. $C_{20}H_{21}N$. Calculated %: N 5.08.

Colorless crystals, soluble in ether, benzene and acetone; difficultly soluble in alcohol.

Mixture with 9-benzyl-6-methyl-1,2,3,4-tetrahydrocarbazole, prepared from N-benzyl-p-toluidine and chlorocyclohexanone [6], gave a strong depression of the melting point. Mixture with a sample of 9-benzyl-8-methyl-1,2,3,4-tetrahydrocarbazole (for preparation see below), m.p. 128-130°, melted with depression (45-63°).

Preparation of 8,9-dimethyl-1,2,3,4-tetrahydrocarbazole. To 1 g of 8-methyl-1,2,3,4-tetrahydrocarbazole [7], 2.5 ml of 66% solution of potassium hydroxide and 5 ml of acetone was added, dropwise and with vigorous stirring, 1.2 g of dimethyl sulfate. The mixture was heated for 1 hour at 70-80°, poured onto ice, filtered and recrystallized from alcohol. Yield, 0.8 g (74%). M.p. 147-149°.

Found %: C 84.14, 84.17; H 8.59, 8.60; N 6.82, 6.85. $C_{14}H_{17}N$. Calculated %: C 84.37; H 8.59; N 7.02.

Preparation of 7,9-dimethyl-1,2,3,4-tetrahydrocarbazole. To 10 g of m-toluidine kept at 140° was added, dropwise, 6 g of chlorocyclohexanone. The reaction mixture was cooled and a mixture of 5 ml of concentrated hydrochloric acid and 30 ml of water was added. The whole was heated to reflux, cooled, and extracted with ether (3 × 30 ml). The extracts were washed with water, followed by washing with sodium carbonate solution and finally again with water and dried over sodium sulfate. After removing the ether the residue was recrystallized from methanol, yielding 4 g (40%) of a substance melting at 129-136°.

By reacting a mixture of 2 g of the substance obtained with 2.8 g of dimethyl sulfate, 6 ml of 66% solution of potassium hydroxide and 10 ml of acetone there was obtained by the method described above after two recrystallizations from methanol, 1.2 g (56%) of 7,9-dimethyl-1,2,3,4-tetrahydrocarbazole, m.p. 102-104°.

Found %: C 84.51, 84.32; H 8.85, 8.69; N 6.99, 7.04. $C_{14}H_{17}N$. Calculated %: C 84.37; H 8.59; N 7.02.

Colorless crystals, soluble in acetone, ether, benzene.

Preparation of 9-benzyl-8-methyl-1,2,3,4-tetrahydrocarbazole. 1 g of 8-methyl-1,2,3,4-tetrahydrocarbazole [7] was reacted with 4 ml of a 66% solution of potassium hydroxide and 1.5 g of benzyl chloride as described previously [6]. Yield of 9-benzyl-8-methyl-1,2,3,4-tetrahydrocarbazole, 0.45 g (32%), m.p. 128-130° (from alcohol).

Found %: N 5.00, 5.01. $C_{20}H_{21}N$. Calculated %: N 5.08.

Colorless crystals soluble in ether, acetone, benzene and ethyl acetate.

7-Carboxy-9-methyl-1,2,3,4-tetrahydrocarbazole. To a mixture of 1 g of 7-carboxy-1,2,3,4-tetrahydrocarbazole [8], 2 ml of 66% solution of potassium hydroxide and 10 ml of acetone was added, dropwise, and with vigorous stirring 2.1 g of dimethyl sulfate. The reaction mixture was heated for 1 hour, poured on ice, and the residue was recrystallized from alcohol. Yield of 7-carbmethoxy-9-methyl-1,2,3,4-tetrahydrocarbazole, 0.49 g (43%), m.p. 126-128°.

Found %: C 74.33; H 7.26. $C_{15}H_{17}O_2N$. Calculated %: C 74.04; H 7.04.

A mixture of 0.2 g of the substance and 30 ml of a 2% alcoholic solution of potassium hydroxide was heated for $1^1/_2$ hours, cooled, the alcohol removed in vacuo, the solution diluted with water, acidified with hydrochloric acid and extracted with ether, the ether extracts being washed with water and dried over sodium sulfate. After removing the ether the residue was recrystallized from glacial acetic acid. Yield of 7-carboxy-9-methyl-1,2,3,4-tetrahydrocarbazole 0.12 g (70%), m.p. 274-276° (decomp.).

Found %: C 73.10; 73.14; H 6.60, 6.62; N 6.18, 6.18. $C_{14}H_{15}O_2N$. Calculated %: C 73.34; H 6.58; N 6.11.

6-Carboxy-9-methyl-1,2,3,4-tetrahydrocarbazole. 1 g of 6-carboxy-1,2,3,4-tetrahydrocarbazole [8] in 2 ml of 66% solution of potassium hydroxide and 10 ml of acetone was reacted with 2.1 g of dimethyl sulfate by the method described above. Yield of 6-carbmethoxy-9-methyl-1,2,3,4-tetrahydrocarbazole, 0.45 g (40%), m.p. 155-157°.

Found %: C 74.18, 74.15; H 7.18, 7.11; N 5.97, 5.89. $C_{15}H_{17}O_2N$. Calculated %: C 74.05; H 7.04; N 5.75.

From 0.2 g of the ester there was obtained, by a method similar to the one described above, 0.13 g (74%) of 6-carboxy-9-methyl-1,2,3,4-tetrahydrocarbazole, m.p. 288-290° (from CH_3COOH, decomp.).

Found %: C 73.30, 73.07; H 6.70, 6.68; N 6.17, 6.15. $C_{14}H_{15}O_2N$. Calculated %: C 73.34; H 6.59; N 6.11.

SUMMARY

1. The formylation of derivatives of 1,2,3,4-tetrahydrocarbazole with diethyl formamide in the presence of phosphorus oxychloride has been investigated.

2. Unsubstituted 1,2,3,4-tetrahydrocarbazole and 2,3-dimethylindole give under these conditions N-formyl derivatives whose structure has been confirmed by hydrolysis.

3. 9-methyl- and 9-benzyl-1,2,3,4-tetrahydrocarbazole form, respectively, 9-methyl- and 9-benzyl-1,2,3,4-tetrahydrocarbazole-7-aldehyde. The structure of these compounds has been proved by oxidation of the former to 9-methyl-7-carboxy-1,2,3,4-tetrahydrocarbazole.

4. On reduction, by the Wolff-Kishner method, of 9-methyl- and of 9-benzyl-1,2,3,4-tetrahydrocarbazole-7-aldehydes there were obtained, respectively, 7,9-dimethyl- and 7-methyl-9-benzyl-1,2,3,4-tetrahydrocarbazole.

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INTERACTION OF DI-m-NITROPHENYLMERCURY AND DI-o-NITROPHENYLMERCURY WITH PHENOLS. XII

F. F. Martynova

A study of the mercuration of phenols with symmetrical mercury derivatives has enabled us to investigate certain regularities in the variation of the velocity of the reactions and in the nature of mercuration of phenols. We were able to show that the velocity of reaction depends on the nature of the substituent in the benzene nucleus of the mercury compound [1]. It was shown that compounds of the type $(x\ C_6H_4)_2Hg$ react with different phenols in different ways, giving rise to mono- and polysubstituted derivatives, depending on the nature of the substituents in the benzene ring of the mercury compound. It was, therefore, of interest to study the mercuration of phenols with mercury derivatives containing one and the same substituent in the benzene ring, but in different positions.

TABLE 1

Phenol	Di-m-Nitrophenylmercury	Di-o-Nitrophenylmercury
	% Hg liberated	% Hg liberated
Pyrogallol	68.70	30.70
Resorcinol	34.93	21.90
p-Aminophenol	10.75	8.79
Hydroquinone	9.50	8.21
p-Chlorophenol	20.52	15.60
2,4-Dichlorophenol	21.76	16.62
p-Cresol	8.63	6.70
Phenol	3.56	0
p-Nitrophenol	3.79	3.52
o-Nitrophenol	0	0
m-Nitrophenol	8.27	5.32
2,4-Dinitrophenol	0	0
2,4,6-Trinitrophenol	0	0
2,4,6-Trichlorophenol	0	0

We have studied the reaction between di-m- and di-o-nitrophenylmercury with the following phenols: phenol, hydroquinone, pyrogallol, p-nitrophenol, 2,4-dinitrophenol, 2,4,6-trichlorophenol, p-chlorophenol, 2,4-dichlorophenol, 2,4,6-trinitrophenol, p-cresol and resorcinol. The reaction takes place at a temperature of 130-150°. The results of the investigation of the reactivity of the different isomers studied have shown that di-m-nitrophenylmercury is more reactive than its ortho-isomer. This is seen from the amount of mercury liberated during the reaction and from the ease of formation of mercurated derivatives of phenols. As will be seen from Table 1 the meta-isomer always yields more mercury on reacting with all the phenols than does the ortho-isomer.

TABLE 2

Reactions of (m-$O_2NC_6H_4)_2Hg$ with Phenols (m-$O_2NC_6H_4$ = R)

Phenol	Compound obtained	Reaction conditions	Hg (%) found	Hg (%) calcd.	Melting point	Appearance of crystals (color)	Yield (%)
p-Nitrophenol	$RHgC_6H_2OH(NO_2)_2$	150° — 3 hours	43.80	43.49	238—240°	Orange	75.00
2,4-Dinitrophenol	$RHgC_6H_2OH(NO_2)_2$	the same	39.80	39.59	253—254	Fine yellow crystals	52.40
2,4,6-Trinitrophenol	$RHgC_6HOH(NO_2)_3$	the same	35.00	35.33	Not below 250°	Light-red	45.20
p-Chlorophenol	$(RHg)_2C_6H_2OHCl$	130° — 3 hours	53.40	53.07	Not below 250°	Brown	36.00
2,4-Dichlorophenol	$RHgC_6H_2OH(Cl)_2$	the same	41.73	41.07	151—153	Dark-red	64.75
2,4,6-Trichlorophenol	$RHgC_6HOH(Cl)_3$	150° — 3 hours	33.84	33.81	Not below 260°	Light-brown	72.27
Resorcinol	$(RHg)_2C_6H_2(OH)_2$	130° — 3 hours	53.40	53.07	Not below 260°	Yellow	40.25
p-Cresol	$RHgC_6H_3OHCH_3$	130—150° — 3 hours	47.05	46.23	Not below 260°	Dark-yellow	98.15

TABLE 3

Reactions of (o-$O_2NC_6H_4)_2Hg$ with Phenols (o-$O_2NC_6H_4$ = R)

Phenol	Compound obtained	Reaction conditions	Hg (%) found	Hg (%) calc.	Melting point	Appearance of crystals (color)	Yield (%)
p-Nitrophenol	$RHgC_6H_3OHNO_2$	150° — 3 hours	43.40	43.49	187—188°	Fine, yellow	57.77
2,4-Dinitrophenol	$RHgC_6H_2OH(NO_2)_2$	the same	40.00	39.89	196—197	Light-yello	67.67
2,4,6-Trinitrophenol	$RHgC_6HOH(NO_2)_3$	the same	36.80	36.83	181—183	Yellow	47.26
p-Chlorophenol	$(RHg)_2C_6H_2OHCl$	150° — 6 hours	52.16	51.81	Not below 260°	Brown	40.00
2,4-Dichlorophenol	$RHgC_6H_2OHCl_2$	150° — 3 hours	42.00	41.24	148—149	Colorless	64.03
2,4,6-Trichlorophenol	$RHgC_6HOHCl_3$	the same	33.49	33.87	210—211	Colorless	75.16
Resorcinol	$(RHg)_2C_6H_2(OH)_2$	130° — 3 hours	53.40	53.07	Not below 250°	Pink	56.76
p-Cresol	$RHgC_6H_3OHCH_3$	150° — 3 hours	46.15	46.63	185	Yellow	71.43

When di-o-nitrophenylmercury is used in the reaction the yield of the mercurated derivatives is satisfactory only when the reaction is carried out at 150°; with the meta-isomer the reaction could be carried out at 130° with excellent yields of the mercurated derivatives.

EXPERIMENTAL

Di-m-nitrophenylmercury was prepared by symmetrization of m-nitrophenylmercury chloride with potassium iodide [2]. Fine crystals, melting not below 220°.

Found %: Hg 45.00. $C_{12}H_8O_4N_2Hg$. Calculated %: Hg 45.04.

m-Nitrophenylmercury chloride was synthesized by the diazo method [3]. Prepared in the form of colorless crystals with m.p. 232-235°.

Found %: Hg 56.50. $C_6H_4O_2NClHg$. Calculated %: Hg 56.04.

Di-o-nitrophenylmercury was obtained by symmetrization of o-nitrophenylmercury chloride with copper in pyridine [4]; pale-yellow needles, m.p. 202-204°. Yield, 84%.

Found %: Hg 44.80. $C_{12}H_8O_4N_2Hg$. Calculated %: Hg 45.04.

o-M-nitrophenylmercury chloride was obtained in 50% yield [3], as colorless crystals, m.p. 185°.

Found %: Hg 56.06. $C_6H_4O_2NClHg$. Calculated %: Hg 56.15.

The mercuration of phenols was carried out, as usual, in sealed ampoules heated in a thermostat. When the reaction was complete there was usually obtained some nitrobenzene, in addition to the mercurated derivatives; the nitrobenzene was removed by means of a micro-pipette. The boiling point was determined by Sivolobov's method. In some experiments the nitrobenzene was removed with steam. The mercury content of the compounds as well as the free mercury were determined by the usual method. The mercury derivatives formed were extracted with solvents. The compounds obtained were in the form of crystals of different colors.

The constants and the elementary analyses of the compounds obtained are given in Tables 2 and 3.

SUMMARY

Phenols can be mercurated with di-m- and di-o-nitrophenylmercury only at temperatures between 130 and 150°, with the formation of crystalline derivatives. In addition to the mercurated derivatives there is formed nitrobenzene. Of the two isomers di-m-nitrophenylmercury is the more active one.

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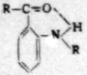
THE INTRAMOLECULAR HYDROGEN BOND AND ULTRAVIOLET ABSORPTION SPECTRA

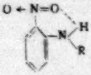
III. ELECTRONIC SPECTRA OF AMINOACETOPHENONES AND SOME OF THEIR DERIVATIVES*

A. E. Lutsky and V. V. Dorofeev

The formation of the hydrogen bond is accompanied by the deformation and, apparently, by a certain amount of superposition of the electronic clouds of the corresponding atoms, i.e. there is a redistribution of electron density [3]. This should bring about a change in the power of the molecules to absorb light in the visible and ultraviolet regions and in the appearance of certain peculiarities in the electronic spectra of compounds containing this type of bonding. These characteristic features arising from intramolecular hydrogen bonding which are based on spectroscopic data for various substituted phenols [1,4], are manifested, in particular, by absorption at considerably longer wavelengths and by the appearance of the anomalous hypsochromic effect in the case of derivatives of the ether-type.

Since the formation of intramolecular hydrogen bonds has also been suggested in the case of the ortho-isomers of the corresponding derivatives of aniline, methyl- and acetylaniline (nitro-, acyl-, etc.) [5]





it was of interest to investigate the effect of the formation of this type of bond on spectra of substituted anilines.

In the table below are given the wavelengths (in A) and the extinction coefficients, ε, characteristic of the maxima and minima of absorption bands of isomeric aminoacetophenones and of their N-acetyl- and N,N-dimethyl-derivatives in iso-octane. Also included are the corresponding values (from the literature) for unsubstituted acetophenone [6] and aniline [7]. The absorption curves are plotted in Figs. 1-3.

As will be seen from the data given, the introduction of the amino group into the acetophenone nucleus in any of the three positions brings about a marked change in its absorption curve (Fig. 1) (qualitatively the change is similar to that which occurs when an OH-group is introduced into the aromatic nucleus), that is, in the case of the ortho- and meta-amino derivatives the intensity of absorption increases considerably in the long-wave absorption region of acetophenone and at the same time there is a marked displacement of the maxima in the short-wave region toward longer wavelengths. The differences between the absorptions of the ortho- and meta- derivatives are the following: (a) o-aminoacetophenone absorbs much more strongly in the long-wave region (the increase in the extinction coefficient of the corresponding band of acetophenone is 166 fold in the case of the ortho-derivative and 78 fold in the case of the meta-derivative); (b) the maximum of the long-wave region is displaced much farther towards long-waves in the case of the o-derivative (a displacement by 300 A with respect to acetophenone) than it is displaced toward shorter wavelengths in the case of the m-derivative (i.e. by 30 A); (c) considerably greater displacement (almost 2,5 times) of the short-wave absorption band of acetophenone toward longer wavelengths. Of a different nature are the changes in the spectrum of the unsubstituted compound if the amino group is introduced into the para-position with respect to the acetyl group. In this case the intensity of absorption in the long-wave region increases only 10 times while the band itself, although it is distinctly displaced towards shorter wavelengths (by 110 A), shows up only as a faint inflection of the curve. At the same time there is a large (807 fold) increase in the intensity of absorption in the range of the middle band of acetophenone, while the short-wave band of the latter has disappeared entirely. As a result of the various changes indicated the absorption curves of o- and m-aminoacetophenones resemble each other with respect to the number and position of the absorption bands, but differ radically from the absorption curve of p-aminoacetophenone.

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* See foregoing article [1, 2].

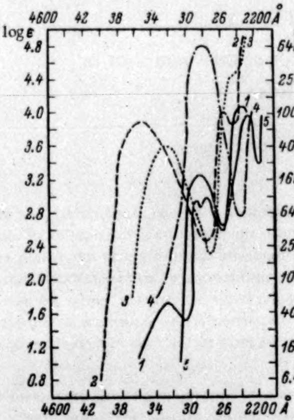


Fig. 1. Absorption curves of aminoacetophenones in iso-octane.
1) Acetophenone in hexane, 2) o-aminoacetophenone ($2\cdot10^{-2}$-$2\cdot10^{-5}$ M.), 3) m-aminoacetophenone ($2\cdot10^{-3}$-$2\cdot10^{-5}$ M.), 4) p-aminoacetophenone ($2\cdot10^{-3}$ -$2\cdot10^{-5}$ M), 5) aniline in hexane.

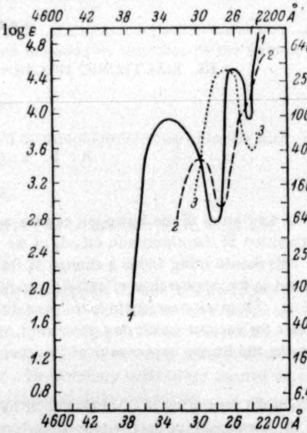


Fig. 2. Absorption curves of N-acetylaminoacetophenones in iso-octane.
1) N-acetyl-o-aminoacetophenone ($2\cdot10^{-3}$-$2\cdot10^{-5}$ M.), 2) N-acetyl-m-aminoacetophenone ($2\cdot10^{-4}$-$2\cdot10^{-5}$ M.), 3) N-acetyl-p-aminoacetophenone (10^{-4}-10^{-5} M.).

The characteristic features of absorption spectra of aminoacetophenones discussed above appear to be general for all compounds of the type $XC_6H_4NH_2$, where X = RCO, COOH COOR (R=alkyl), $CONH_2$, NO_2 [8], but appear to be absent in the cases of compounds in which X = CH_3, NH_2, $N(CH_3)_2$ [9]. In the latter case the absorption spectra of all isomers are similar, while the wavelength of the absorption maxima in the long-wave region decreases in the order para- meta- ortho-, in contrast to what is observed in the case of compounds of the former type.

Substitution of the hydrogen of the amino group in aminoacetophenones for the acetyl group (Fig. 2) does not bring about any change in the absorption curves. The character of the curves of the three isomers remains the same as that of the corresponding aminoacetophenones, i.e. o- and m-N-acetylaminoacetophenones also exhibit the same two absorption bands as the corresponding aminoacetophenones, while p-acetylaminoacetophenone shows only one strong band in the middle ultraviolet. Also, the differences between the absorption curves of o- and m-aminoacetophenones noted above are again observed in the case of the curves of the N-acetylaminoacetophenones both qualitatively and quantitatively.

In the case of N,N-dimethylaminoacetophenones (Fig. 3) we again find the resemblance between the absorption curves of the ortho- and meta-isomers, on the one hand, and the differences between these and that of the para-isomer. However, the differences between the absorption curves of the ortho- and meta-isomers indicated above are no longer found in the case of these two isomers of N,N-dimethylaminoacetophenones. The maximum

Maxima and Minima of Absorption Bands in Iso-octane

Compound		Absorption maximum						Absorption minimum			
		λ	ε	λ	ε	λ	ε	λ	ε	λ	ε
$NH_2C_6H_4COCH_3$	o-	3550	8320	—	—	2545	10000	2770	280	2440	7420
	m-	3220	3900	—	—	2435	30100	2730	190	—	—
	p-	3140 (Bend)	500	2850	64000	—	—	—	—	2445	575
$CH_3CONHC_6H_4COCH_3$	o-	3310	8520	—	—	2605	33200	2815	590	2440	8920
	m-	2975	3170	—	—	2500 (Bend)	11300	2745	910	—	—
	p-	—	—	2725	31700	—	—	—	—	2400	3900
$(CH_3)_2NC_6H_4COCH_3$	o-	3730 (Bend) 3225	775 5130	—	—	2550	20900	2905	1910	—	—
	m-	3470	4000	—	—	2625	31700	2890	175	2575	20000
	p-	—	—	3080	66100	—	—	—	—	2590	775
$C_6H_5COCH_3$		3250	50	2865 2770	800 1000	2370	13000	3040	35	2600 2570	400
$C_6H_5NH_2$		—	—	2880	1780	2300	7950	—	—	—	—

of the long-wave band of o-N,N-dimethylaminoacetophenone is found to lie at shorter wavelengths than the corresponding maximum of the meta-isomer. The same directional shift is observed in the case of the maximum of the short-wave band: the maximum of the ortho-isomer is found to lie at a wavelength 75 A shorter than that at which the corresponding maximum of the meta-isomer is found.

In the case of o-N,N-dimethylaminoacetophenone there appears, at the long-wave edge of the spectrum, an inflection in the curve at λ3730 A which has not been observed in the case of the compounds discussed above. The intensity of absorption in the region of this inflection is low and is practically the same as that of a similar inflection in the curve of p-N,N-dimethylaminoacetophenone (Fig. 3).

A comparison of the absorption curves of corresponding isomers of amino-,N-acetylamino- and N,N-dimethylaminoacetophenones (Figs. 4-6) shows the following features (a) as we pass from NH_2 to $NHCOCH_3$ the long-wave band in the case of all isomers is shifted towards shorter wavelengths (shifts of maxima vary from 125 - 250 A), while the short-wave band of the ortho and meta isomers are shifted closer to longer wavelengths by approximately 60 A; transition from NH_2 to $N(CH_3)_2$ is accompanied by a marked and almost parallel shifting of the whole absorption curve toward longer wavelengths (the maxima are shifted by about 200 A). However, the latter shifting is observed only in the case of m- and p-aminoacetophenones; in the case of o-aminoacetophenone the change from NH_2 to $N(CH_3)_2$ has the opposite effect, namely, it brings about a fairly large shift of the maximum of the long-wave band toward shorter wavelengths (a shift of 325 A); the maximum of the short-wave band of o-aminoacetophenone is not affected by a change from the amino to the dimethylamino group and only the long-wave edge of the curve is shifted toward longer wave-lengths, as is also the case with the curve of m-aminoacetophenone. As a result of this peculiar behavior of o-aminoacetophenone the wavelengths of the absorption maxima of the long-wave bands of the ortho-isomers decrease in the order $NH_2 > NHCOCH_3 > N(CH_3)_2$, and in the case of the meta-and para-isomers in the order $N(CH_3)_2 > NH_2 > NHCOCH_3$.

Thus, ultraviolet absorption by o-amino- and o-N-acetylaminoacetophenones exhibits the same features in neutral solutions as are observed in the case of o-hydroxyacetophenone and other ortho-substituted phenols which exhibit intramolecular hydrogen bonding [10]. Just as is the case with the latter compounds, the absorption bands of the ortho-isomers are shifted much farther toward longer wavelengths than in the case of

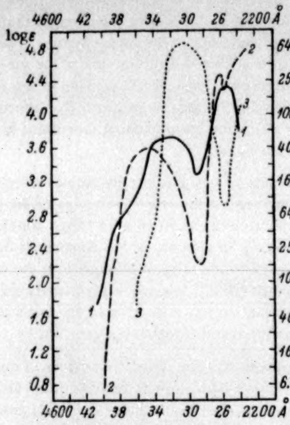


Fig. 3. Absorption curves of N,N-dimethylaminoacetophenones in iso-octane.
1) N,N-dimethyl-o-aminoacetophenone ($2 \cdot 10^{-3}$-$2 \cdot 10^{-5}$ M.), 2) N,N-dimethyl-m-aminoacetophenone ($2 \cdot 10^{-2}$-$2 \cdot 10^{-5}$ M.), 3) N,N-dimethyl-p-aminoacetophenone ($2 \cdot 10^{-3}$-$2 \cdot 10^{-5}$ M.).

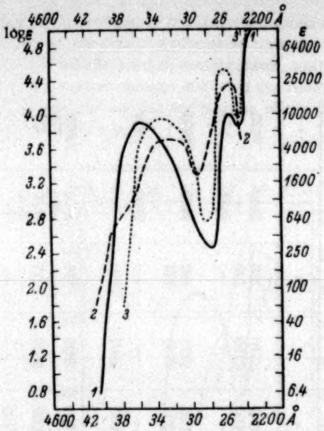


Fig. 4. Absorption curves of o-aminoacetophenones in iso-octane.
1) o-aminoacetophenone ($2 \cdot 10^{-2}$-$2 \cdot 10^{-5}$ M.), 2) N,N-dimethyl-o-aminoacetophenone ($2 \cdot 10^{-3}$-$2 \cdot 10^{-5}$ M.), 3) N-acetyl-o-aminoacetophenone ($2 \cdot 10^{-3}$-$2 \cdot 10^{-5}$ M.).

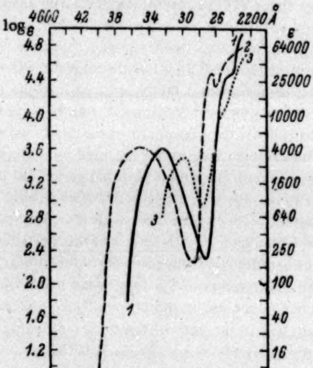


Fig. 5. Absorption curves of m-aminoacetophenones in iso-octane.
1) m-Aminoacetophenone ($2 \cdot 10^{-3}$-$2 \cdot 10^{-5}$ M.), 2) N,N-dimethyl-m-aminoacetophenone ($2 \cdot 10^{-2}$-$2 \cdot 10^{-5}$ M.), 3) N-acetyl-m-aminoacetophenone ($2 \cdot 10^{-4}$-$2 \cdot 10^{-5}$ M.).

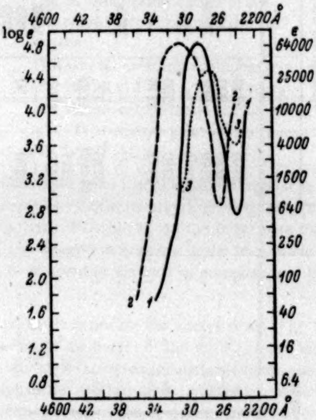


Fig. 6. Absorption curves of p-aminoacetophenones in iso-octane.
1) p-aminoacetophenone ($2 \cdot 10^{-3}$-$2 \cdot 10^{-5}$ M.), 2) N,N-dimethyl-p-aminoacetophenone ($2 \cdot 10^{-2}$-$2 \cdot 10^{-5}$ M.), 3) N-acetyl-p-aminoacetophenone (10^{-4}-10^{-5} M.).

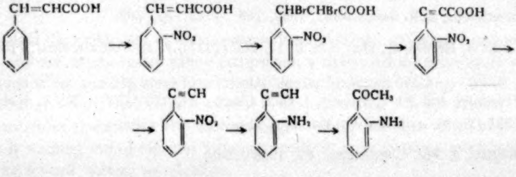
the meta- and, particularly, the para-isomers. In the case of o-aminoacetophenone, substitution of the hydrogens of the amino group by methyl groups effects a marked shifting of the absorption bands toward shorter wavelengths, an effect which is also observed in the case of the formation of ethers with the corresponding ortho-substituted phenols. The greater extent of these shifts may be partly due to the cumulative effect resulting from the protrusion of the functional groups $-N(CH_3)_2$ and $COCH_3-$ from the plane of the molecule [11].

EXPERIMENTAL

The absorption spectra were recorded on the SP-2 spectrophotometer made by the Leningrad Works. A spark discharge between iron-tungsten electrodes was used as the light source.

Iso-octane was purified by means of two continuous extractions (each of 12 hours duration) with conc. H_2SO_4, followed by washing with water, extraction with alkaline and finally with acid solution of potassium permanganate. After washing with distilled water the iso-octane was dried over calcium chloride followed by drying over metallic sodium, and was finally distilled on a column with indentations. The fraction collected at 99.3° was transparent up to 2100 A on exposure for ten seconds through a layer 5 cm thick.

o-Aminoacetophenone was prepared from cinnamic acid according to the following scheme:



The various other compounds were prepared according to literature data [12], with some modifications. The yield of o-aminoacetophenone amounted to about 8% on the cinnamic acid taken. It was purified by fractionation; b.p. 120° [8].

m-Aminoacetophenone was obtained from m-nitroacetophenone which, in turn, was obtained by nitration of acetophenone. It was purified by recrystallization from water or aqueous alcohol and was obtained as light yellow flakes, m.p 99.2°. p-Aminoacetophenone was obtained by acetylation of acetanilide with acetyl chloride [13] and recrystallization from water. Colorless prisms, m.p 106°.

The isomeric N-acetylaminoacetophenones were obtained from the corresponding aminoacetophenones and acetic anhydride. They were purified by recrystallization from water. Colorless needles; m.p: ortho- 77°, meta- 129° and para- 166°.

Isomeric N,N-dimethylaminoacetophenones were obtained from the corresponding aminoacetophenones by heating the latter with methyl iodide [14]. The ortho-isomer was purified by steam-distillation followed by fractionation in vacuo. The meta- and para-isomers were purified through the hydrochloride, followed by recrystallization from a mixture of diethyl ether and petroleum ether. N,N-Dimethyl-o-amino-acetophenone was obtained as a faintly yellow oil, b.p. 105° [5]; N,N-dimethyl-m-aminoacetophenone – colorless needles, m.p. 41°, and N,N-dimethyl-p-aminoacetophenone as colorless crystals, m.p. 106°.

SUMMARY

1. Ultraviolet absorption spectra of isomeric amino, N-acetylamino- and N,N-dimethylaminoacetophenones in iso-octane have been investigated.

2. It has been shown that while o- and m-amino and o- and m-N-acetylaminoacetophenones give essentially similar absorption curves, they differ from each other in that the ortho-isomers absorb at considerably longer wavelengths. Also, unlike in the case of m-aminoacetophenone, the long-wave absorption band of o-aminoacetophenone is shifted toward shorter wavelengths when the amino-group becomes a N,N-dimethylamino-group.

3. The characteristic features of the absorption spectra of o-amino and of o-N-acetylaminoacetophenones

can be attributed to the presence of intramolecular hydrogen bonds in these compounds.

4. A confirmation has been obtained for the general character, already observed in the case of derivatives of phenols, of the influence of the intramolecular hydrogen bond on ultraviolet absorption spectra.

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THE INTRAMOLECULAR HYDROGEN BOND AND ULTRAVIOLET ABSORPTION SPECTRA

IV. THE EFFECT OF SOLVENTS ON ELECTRONIC SPECTRA OF AMINO-ACETOPHENONES AND OF SOME OF THEIR DERIVATIVES

A. E. Lutsky and V. V. Dorofeev

Substituted phenols the molecules of which contain intramolecular hydrogen bonds exhibit, in contrast to their isomers, ethers and the unsubstituted parent compounds, a characteristic behavior in solvents the molecules of which contain groups which readily enter into intermolecular hydrogen bonding. While in the case of the latter compounds a change from a hydrocarbon solvent to one containing a hydroxyl group brings about a distinct shift of the entire ultraviolet absorption curve toward longer wavelengths, this effect is either entirely absent in the case of compounds forming intramolecular hydrogen bonds, or there is only a relatively small displacement of the long-wave band toward shorter wavelengths.

The hypothesis that the characteristic features of ultraviolet spectra of o-amino- and o-N-acetylamino-acetophenones are due to the presence in their molecules of intramolecular hydrogen bonds [2] may, consequently, be confirmed by investigating the effect on their spectra of solvents which readily enter into the formation of intermolecular hydrogen bonds. In view of this we have determined the spectra of isomeric amino-, N-acetylamino- and N,N-dimethylaminoacetophenones in diethyl ether, ethanol and water as solvents.

Absorption Spectra in Diethyl Ether

The absorption curves obtained for the three isomeric aminoacetophenones (Fig. 1) are almost identical with those reported in the literature [3]. A comparison of the data for the corresponding maxima and minima of absorption bands (Table 1 and Figs. 1-3) reveals that all the features of absorption which have been observed in the case of all these compounds in iso-octane, are found unaltered when diethyl ether is used as the solvent. In this case the absorption bands of m- and p-amino and N-acetylaminoacetophenones are shifted toward long waves (the shifts of the maxima are of the order of 60-130 A), and at the same time there is some reduction in the intensity of absorption. In the case of the ortho isomers of these compounds this effect, due to ether, is absent (Table 4).

Just as in the case of iso-octane, we again find that in diethyl ether the long-wave bands are shifted toward shorter wavelengths as we pass from the NH_2 to the $NHCOCH_3$ group. Also, the intensity of absorption is somewhat lower in the case of the ortho and meta isomers while it increases slightly in the case of the para isomer.

When ether is used as the solvent the long-wave band of N,N-dimethylaminoacetophenones suffers only a neglibly small shift as compared with that observed in iso-octane (Table 4); the shift is of the same order in the case of both the meta and the ortho isomers. Thus, the specific behavior of the ortho isomers observed previously is no longer manifest in the case of N,N-dimethylaminoacetophenones. In the case of the para isomer of N,N-dimethylaminoacetophenone the change from iso-octane to diethyl ether as solvent brings about a noticeable displacement of the long-wave band toward longer wavelengths, although it is smaller than that observed in the case of p-amino- and p-N-acetylaminoacetophenones.

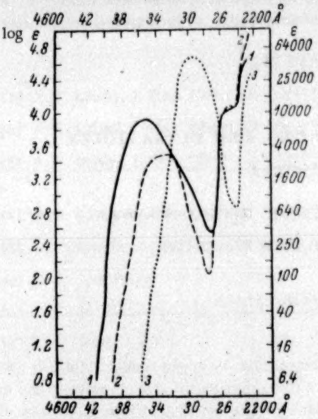


Fig. 1. Absorption spectra of aminoacetophenones in diethyl ether ($2 \cdot 10^{-2} - 2 \cdot 10^{-5}$ m).
1) o-aminoacetophenone, 2) m-aminoacetophenone, 3) p-aminoacetophenone.

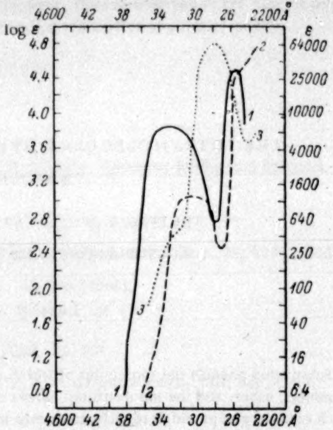


Fig. 2. Absorption spectra of N-acetylaminoacetophenones in diethyl ether.
1) N-acetyl-o-aminoacetophenone($2 \cdot 10^{-2} - 2 \cdot 10^{-5}$ m), 2) N-acetyl-m-aminoacetophenone ($2 \cdot 10^{-2} - 2 \cdot 10^{-5}$ m.), 3) N-acetyl-p-aminoacetophenone ($2 \cdot 10^{-3} - 2 \cdot 10^{-5}$ m).

Absorption Spectra in Ethanol

Absorption curves obtained for aminoacetophenones in 95% ethanol are basically identical with similar curves obtained by Grammaticakis [4] and differ somewhat (in the case of the para isomer) from those obtained by Kumler [5]. As will be seen from Figs. 4-6, the nature and mutual relationships of absorption curves of the compounds in question are essentially the same in ethanol as in iso-octane (Table 2). In ethanol, in contrast to what is observed in iso-octane (Table 4), the maxima of the long-wave bands of the three isomeric aminoacetophenones are shifted towards longer wavelengths; however, in the case of o-aminoacetophenone the shift is comparatively small ($^1/_2 - ^1/_4$ as large, respectively, as that observed in the case of m- and p-aminoacetophenones). At the same time the intensity of absorption in the long-wave region in the case of o-aminoacetophenone remains practically unaltered while it is reduced by half in the case of m- and p-aminoacetophenones. In ethanol the maximum of the short wave band of o-aminoacetophenone is shifted by only a small amount as compared with its position in iso-octane; on the other hand, this maximum in the case of the meta isomer is shifted toward longer wavelengths by an amount nearly equal to that observed for the long-wave band.

As we change over from iso-octane to ethanol as the solvent we find that the maximum of the long-wave bands of m-N-acetylaminoacetophenone and of the p-isomer (and in the case of the meta isomer also the maximum of the short-wave band) is shifted toward longer wavelengths, just as in the case of the corresponding aminoacetophenones. A different behavior is observed in the case of o-N-acetylaminoacetophenone. In this case, in contrast to what is observed for the m- and p-isomers, the maxima of the bands indicated are shifted, though by a small amount, toward shorter wavelengths (Table 4).

With ethanol as the solvent there is observed a shift of the long-wave band maximum toward longer wavelengths in the case of the three isomeric N,N-dimethylaminoacetophenones, the shift being greatest in the case of the ortho isomer. As with the meta and para isomers, the intensity of absorption in this region, as compared with that in iso-octane, is reduced by a maximum amount in the case of o-N,N-dimethylaminoacetophenone. The maximum of the shortwave band in the case of the ortho isomer is also displaced toward longer wavelengths.

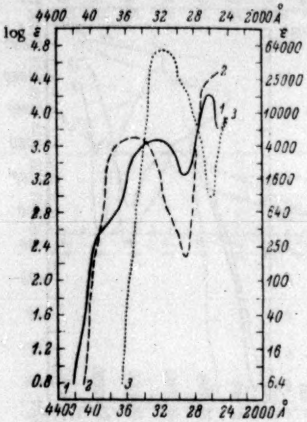


Fig. 3. Absorption spectra of N,N-dimethylaminoacetophenones in diethyl ether ($2 \cdot 10^{-2} - 2 \cdot 10^{-5}$ m.).
1) N,N-dimethyl-o-aminoacetophenone, 2) N,N-dimethyl-m-aminoacetophenone, 3) N,N-dimethyl-p-aminoacetophenone.

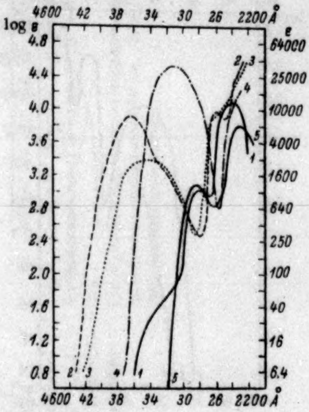


Fig. 4. Absorption spectra of aminoacetophenones in ethanol ($2 \cdot 10^{-2} - 2 \cdot 10^{-5}$ m.).
1) acetophenone in ethanol ($2 \cdot 10^{-2} - 2 \cdot 10^{-5}$ m.), 2) o-aminoacetophenone, 3) m-aminoacetophenone, 4) p-aminoacetophenone, 5) aniline in ethanol (Grammaticakis,[4]).

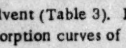
Absorption Spectra in Water

The same qualitative changes in absorption spectra of the compounds under investigation as those found in ethanol are again observed in water as the solvent. The shifting of the maximum of the long-wave band of the ortho isomer of aminoacetophenone is from $^1/_4$ to $^1/_9$ as large as that observed in the case of the meta and para isomers. In the case of o-N-acetylaminoacetophenone the maximum of the long-wave band is shifted toward shorter wavelengths, in contrast to what is observed for the meta and para isomers where this maximum is shifted toward longer wavelengths, changes which have already been found in ethanol as the solvent. In the case of N,N-dimethylaminoacetophenones the ortho isomer no longer exhibits any difference in behavior, as compared with the other two isomers, as we pass from iso-octane to water as the solvent. Apart from the shifts indicated, the mutual relationship of the absorption curves of isomeric amino- and N-acetylaminoacetophenones (Figs. 7 and 8) is the same as that found in iso-octane as solvent (Table 3). It is only in the case of N,N-dimethylaminoacetophenones that the mutual relationship of absorption curves of the three isomers is altered somewhat by comparison with that found in iso-octane, the difference being due to the comparatively greater shift, in water, of the longwave band of the ortho isomer: the latter absorbs at longer wavelengths than does the meta isomer (Fig. 9).

Thus, o-amino- and particularly o-N-acetylaminoacetophenone exhibit the same features in their absorption spectra in different solvents as those which have been observed in the case of substituted phenols containing intramolecular hydrogen bonds. It is obvious that in hydroxylic solvents the meta and para isomers as well as the three isomers of N,N-dimethylaminoacetophenones will have their absorption bands shifted toward longer wavelengths as a result of the formation of intermolecular hydrogen bonds of the types:

$$>C{=}O \ldots H{-}O{-}R$$

(I)



$$>N{-}H \ldots O\begin{matrix} \diagup R \\ \diagdown R_1 \end{matrix}$$

(II)

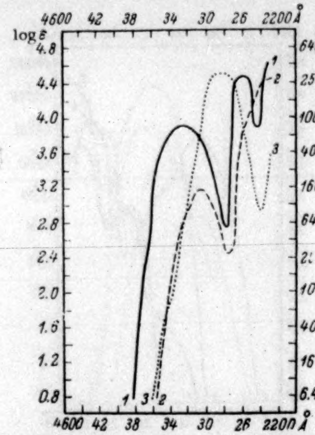


Fig. 5. Absorption Spectra of N-Acetylaminoacetophenones in ethanol ($2\cdot10^{-2}-2\cdot10^{-5}$ m). 1) N-acetyl-o-aminoacetophenone, 2) N-acetyl-m-aminoacetophenone, 3) N-acetyl-p-aminoacetophenone.

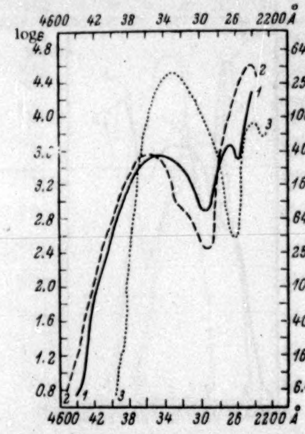


Fig. 6. Absorption Spectra of N,N-dimethylaminoacetophenones in ethanol ($2\cdot10^{-2}-2\cdot10^{-5}$ m). 1) N,N-dimethyl-o-aminoacetophenone, 2) N,N-dimethyl-m-aminoacetophenone, 3) N,N-dimethyl-p-aminoacetophenone.

The comparatively slight displacement toward longer wavelengths of the maximum of the long-wave band of o-aminoacetophenone in hydroxylic solvents may, therefore, be due to the formation of intermolecular hydrogen bonds through the free hydrogen atom of the amino group (type II).

The bathochromic effect of diethyl ether could also be explained by the formation of intermolecular hydrogen bonds of type (II) in which the hydrogen atoms of the amino- and N-acetylamino groups might take part. This assumption might be supported by the observed smaller shift of the long-wave band of N,N-dimethylaminoacetophenones in ether as solvent. However, the influence of ether is still quite distinct in the case of the para isomer of N,N-dimethylaminoacetophenone, a fact which would indicate that in the case of some compounds the interaction between molecules of solvent and solute due to van der Waals' forces may in itself be sufficiently strong to bring about a marked shifting of absorption bands.

EXPERIMENTAL

The methods followed in the recording of spectra, the synthesis and purification of the compounds investigated have been described previously [2]. The solvents were purified as follows: diethyl ether was shaken for 8 hours with a 10% solution of sodium hydroxide, dried over calcium chloride and metallic sodium, and was then slowly fractionated over sodium wire using a column with indentations. The fraction collected (34.6°) was transparent up to 2000 A when exposed for 10 seconds in a layer 5 cm thick. Ethyl alcohol was refluxed for half an hour over potassium hydroxide crystals (20 g/l) and distilled on a Hempel column. The collected middle fraction (78°) was transparent up to 2000 A. Water was distilled twice with potassium permanganate (2-3 crystals per 0.75 liter and was found to be transparent up to 2100 A when exposed for 10 seconds in a layer 5 cm thick.

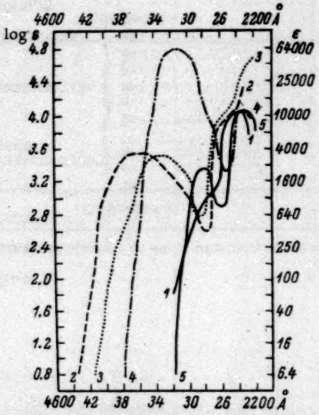


Fig. 7. Absorption Spectra of Aminoacetophenones in water ($2 \cdot 10^{-2}-2 \cdot 10^{-5}$ m).

1) acetophenone in water [6], 2) o-aminoacetophenone, 3) m-aminoacetophenone, 4) p-aminoacetophenone, 5) aniline in water [7]

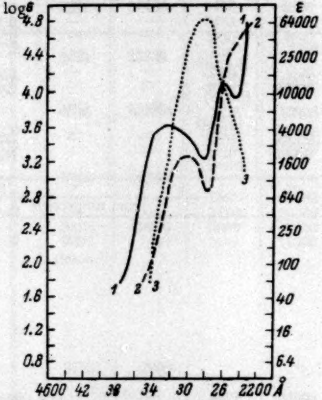


Fig. 8. Absorption Spectra of N-Acetylaminoacetophenones in water ($2 \cdot 10^{-3}-2 \cdot 10^{-5}$ m).

1) N-acetyl-o-aminoacetiphenone, 2) N-acetyl-m-aminoacetophenone, 3) N-acetyl-p-aminoacetophenone.

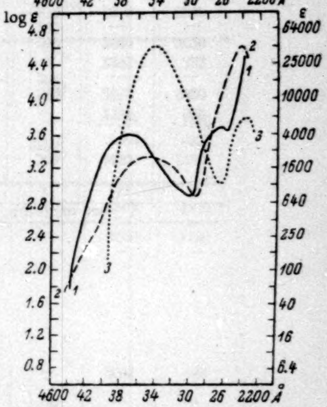


Fig. 9. Absorption Spectra of N,N-dimethylaminoacetophenones in water ($2 \cdot 10^{-3}-2 \cdot 10^{-5}$ m).

1) N,N,-dimethyl-o-aminoacetophenone, 2) N,N-dimethyl-m-aminoacetophenone, 3) N,N-dimethyl-p-aminoacetophenone.

TABLE 1

Maxima and Minima (λ in A) of Absorption Bands in Diethyl Ether

Compound		Maximum band						Minimum band			
		λ	ε	λ	ε	λ	ε	λ	ε	λ	ε
$H_2NC_6H_4COCH_3$	o-	3555	8320	—	—	2560 (Bend)	10800	2758	372	—	—
	m-	3330	3170	—	—	2497 (Bend)	12040	2775	115	—	—
	p-	—	—	2975	49000	—	—	—	—	2460	760
$CH_3CONHC_6H_4COCH_3$	o-	3325	7080	—	—	2575	31700	2805	589	—	—
	m-	3040	1130	—	—	2550 (Bend)	30100	2730	296	—	—
	p-	3260 (Bend)	399	2830	63100	—	—	—	—	2425	4790
$(CH_3)_2NC_6H_4COCH_3$	o-	3830 (Bend) 3240	500 4900	—	—	2630	16300	2925	1780	2495	6020
	m-	3490	4900	—	—	2605 (Bend)	27000	2907	195	—	—
	p-	—	—	3155	53800	—	—	—	—	2605	955

TABLE 2

Maxima and Minima (λ in A) of Absorption Bands in Ethanol

Compound		Maximum band						Minimum band			
		λ	ε	λ	ε	λ	ε	λ	ε	λ	ε
$H_2NC_6H_4COCH_3$	o-	3620	7780	—	—	2570	10000	2785	300	2470	2780
	m-	3365	2000	—	—	2550 (Bend)	10000	2865	3720	—	—
	p-	—	—	3105	31700	—	—	—	—	2555	600
$CH_3CONHC_6H_4COCH_3$	o-	3270	8320	—	—	2600	31000	2797	590	2450	8920
	m-	3075	1590	—	—	2600	7780	2755	295	—	—
	p-	—	—	2830	33200	—	—	—	—	2395	892
$(CH_3)_2NC_6H_4COCH_3$	o-	3490	3470	—	—	2670	4680	2975	760	2580	3020
	m-	3605	3470	—	—	2417	39900	2970	280	—	—
	p-	—	—	3315	32400	2405	8130	2645	370	2320	5890
$C_6H_5COCH_3$ [6]		3210 (Bend)	50	2770	1000	2420	12500	—	—	—	—

TABLE 3

Maxima and Minima (λ in A) of Absorption Bands in Water

Compound		Maximum band						Minimum band			
		λ	ε	λ	ε	λ	ε	λ	ε	λ	ε
$H_2NC_6H_4COCH_3$	o-	3580	3550	—	—	2580 (Bend)	7780	2770	372	—	—
	m-	3335	3170	—	—	2540 (Bend)	10000	2850	600	—	—
	p-	—	—	3115	56300	2325	10800	—	—	2525	1910
$CH_3CONHC_6H_4COCH_3$	o-	3230	4270	—	—	2600	12900	2805	1780	2460	8920
	m-	3015	1870	—	—	2580 (Bend)	18000	2770	760	—	—
	p-	—	—	2815	63100	—	—	—	—	—	—
$(CH_3)_2NC_6H_4COCH_3$	o-	3750	3990	—	—	2660	5000	3010	777	2595	4370
	m-	3550	2140	—	—	2420	39900	2955	760	—	—
	p-	—	—	3435	39900	2380	6300	—	—	2660	1130
$C_6H_5COCH_3$		3325	50	2800 (Bend)	1150	2495	11000	—	—	—	—

TABLE 4

Absorption Band Shift Difference $\Delta\lambda = \lambda_{\text{solvent}} - \lambda_{\text{iso-octane}}$ and $\frac{\epsilon_{\text{solvent}}}{\epsilon_{\text{iso-octane}}}$

Isomer	Solvent	$NH_2C_6H_4COCH_3$		$CH_3CONHC_6H_4COCH_3$		$(CH_3)_2NC_6H_4COCH_3$	
		Δλ	$\frac{\epsilon_{\text{solvent}}}{\epsilon_{\text{iso-octane}}}$	Δλ	$\frac{\epsilon_{\text{solvent}}}{\epsilon_{\text{iso-octane}}}$	Δλ	$\frac{\epsilon_{\text{solvent}}}{\epsilon_{\text{iso-octane}}}$
Ortho-	$(C_2H_5)_2O$	+ 5	1.0	+ 15	0.8	+ 15	0.9
	C_2H_5OH	+ 70	0.9	− 40	1.0	+265	0.6
	H_2O	+ 30	0.4	− 80	0.5	+525	0.8
Meta-	$(C_2H_5)_2O$	+110	0.8	+ 65	0.3	+ 20	1.2
	C_2H_5OH	+145	0.5	+100	0.5	+135	0.8
	H_2O	+115	0.8	+ 40	0.6	+ 80	0.5
Para-	$(C_2H_5)_2O$	+130	0.7	+105	2.0	+ 75	0.8
	C_2H_5OH	+260	0.5	+105	1.0	+235	0.5
	H_2O	+270	0.9	+ 90	2.0	+355	0.6

SUMMARY

1. Ultraviolet absorption spectra of isomeric amino-, N-acetylamino- and N,N-dimethylaminoacetophenones in diethyl ether, ethanol and water have been determined.

2. It has been established that in the case of o-amino- and o-N-acetylaminoacetophenones the effect of solvents on electronic spectra of these compounds is such as to suggest, again, the presence of intramolecular hydrogen bonds.

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* Original Russian pagination. See C.B. Translation.

REACTIONS OF HYDRAZINE DERIVATIVES

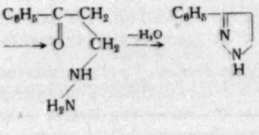
XIII. SYNTHESIS OF PYRAZOLINES BY THE MANNICH REACTION

A. N. Kost and V. V. Ershov

Usually the Mannich reaction consists of the condensation of ammonia, a primary or a secondary amine with formaldehyde and a compound which has reactive hydrogen atoms. The use of primary amines and ammonia in this reaction always leads to certain complications, as the secondary or primary amines formed are in their turn capable of giving various side products [1].

We used hydrazine in the Mannich reaction, condensing it with formaldehyde and various aliphatic-aromatic ketones. Naturally, in this case all the complications of the reaction are even more probable, as hydrazine has 4 hydrogen atoms and, furthermore, it reacts readily with the carbonyl group of the ketone and formaldehyde. We discovered however, that the reaction proceeds normally with hydrazine, but the β-hydrazinoketone formed splits out water and converts to the corresponding pyrazoline. Thus, if acetophenone is heated with paraformaldehyde and hydrazine hydrochloride in ethyl alcohol solution, after making the mixture alkaline, 3-phenylpyrazoline may be isolated (in 28% yield). It should be noted that acetophenone with hydrazine hydrochloride does not form either hydrazone or azine (after boiling acetophenone with hydrazine hydrochloride in ethyl alcohol for 2 hours, we recovered the original ketone), but it reacts in the cold with free hydrazine. In connection with this, we consider that the primary process is not the formation of acetophenone hydrazone which is then condensed with formaldehyde, but the usual Mannich reaction, giving first the β-hydrazinoketone with subsequent cyclization into pyrazoline, when made alkaline.

$$C_6H_5COCH_3 + CH_2O + H_2NNH_2 \cdot HCl \xrightarrow{-H_2O} C_6H_5COCH_2CH_2NHNH_2 \cdot HCl \xrightarrow{NaOH}$$

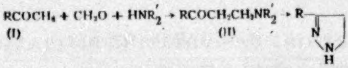


Similarly, we obtained 3-(2,5-dimethylphenyl)-pyrazoline from 2,5-dimethylacetophenone, formaldehyde and hydrazine hydrochloride. If the reaction is carried out with butyrophenone, then the corresponding pyrazoline is formed in very small yield. However, the classical Mannich reaction (with dimethylamine) in the case of butyrophenone, also proceeds under more drastic conditions as we had shown previously [2]. We had tried to carry out the reaction with hydrazine hydrochloride at a higher temperature (boiling in dioxane), but complete resinification of the reaction mixture occurred.

All the pyrazolines and their derivatives obtained by this method were identical with the pyrazolines we had obtained from β-diethylaminoketones and hydrazine [2, 3].

The method described for the formation of the pyrazoline ring has not been recorded previously by other authors and is new, but due to the series of complicating processes its use cannot be recommended for preparative purposes. In connection with this, we continued to develop the method of preparing 3-arylpyrazolines from β-dialkylaminoketones for the purpose of studying the effect of the dialkylamino group on the pyrazoline yield. It was found that the reaction proceeded more readily for β-diethylaminoketones than for β-dimethylaminoketones (see table), but the Mannich reaction itself proceeded more readily with dimethylamine and therefore, the total yield is greater in most cases. The synthesis can be carried out without isolating the β-dimethylaminoketone in the pure form and, after aminomethylation, the reaction mixture can be added at once to the hydrazine hydrate. Apparently, the last variant is the most efficient.

The Effect of the Radicals R and R' on the Yields of 3-Arylpyrazolines by the Scheme



R	R'	Yield (in %)		
		based on (I)	based on (II)	without isolating (II)
C_6H_5	CH_3	70.8	78.3	70.4
	C_2H_5	40	89	—
p-$CH_3C_6H_4$	CH_3	68.8	72.6	71.8
	C_2H_5	53.4	93	—
p-$CH_3OC_6H_5$	CH_3	58.7	68	55.3
	C_2H_5	65	86	—
2,5-$(CH_3)_2C_6H_3$	CH_3	40.3	61.1	61.7
	C_2H_5	38.4	64.1	—

EXPERIMENTAL

Mannich Bases. A mixture of 60 g of acetophenone, 20 g of paraformaldehyde, 53 g of dimethylamine hydrochloride and 80 ml of ethyl alcohol was boiled for 2.5 hours and after cooling, it was diluted with two volumes of water, washed free from unreacted ketone with ether and made alkaline with 40% sodium hydroxide solution under ether; the free base was extracted into the ether. The ether solution was dried, the unreacted dimethylamine distilled off with part of the ether and a current of dry hydrogen chloride passed through the residual solution until all the aminoketone had separated out. The yield of β-dimethylaminopropiophenone hydrochloride was 100 g (93%), m.p. 151-153°. Literature data [4]: yield 70%, m.p. 152-153°.

Similarly, from 26.8 g of p-methylacetophenone, 7 g of paraformaldehyde and 20 g of dimethylamine hydrochloride, we obtained 39.8 g (88%) of β-dimethylamino-p-methylpropiophenone hydrochloride, m.p. 158-159°; from 30 g of p-methoxyacetophenone we obtained 42 g (85%) of β-dimethylamino-p-methoxypropiophenone hydrochloride, m.p. 179° (literature data: m.p. 181° [5]) and from 29.6 g of 2,5-dimethylacetophenone we obtained 31.6 g (66%) of β-dimethylamino-2,5-dimethylpropiophenone hydrochloride, m.p. 153°.

3-Phenylpyrazoline. a) A solution of 106.5 g of β-dimethylaminopropiophenone hydrochloride in 250 ml of methyl alcohol was added over 1.5 hours with vigorous stirring to 75 ml of hydrazine hydrate in the presence of 50 ml of 40% sodium hydroxide solution and 100 ml of methyl alcohol heated to 45-50°. The mixture was boiled for 40 minutes, the bulk of the methyl alcohol distilled off and the residue extracted 3 times with ether. The ether extracts were dried with anhydrous potash, the ether distilled off and the 3-phenylpyrazoline isolated by vacuum distillation in a stream of nitrogen. The yield was 57 g (78.3%), b.p. 130-131° at 5 mm, m.p. 44°, N-nitroso derivative, m.p. 154-155°. The constants agree with those that we gave previously [3].

b) A mixture of 60 g of acetophenone, 20 g of paraformaldehyde, 53 g of dimethylamine hydrochloride and 80 ml of ethyl alcohol was boiled for 2.5 hours, then 150 ml of methyl alcohol and 40 ml of water was added to it and the reaction with hydrazine performed by the method described above. The yield of 3-phenylpyrazoline was 51.5 g (70.4% calculated on acetophenone).

c) A mixture of 24 g of acetophenone, 9 g of paraformaldehyde, 26.4 g of hydrazine hydrochloride and 40 ml of ethyl alcohol was boiled for two hours on an air bath with periodic shaking. The cold mass was made alkaline with 40% sodium hydroxide solution and extracted three times with ether. The ether solution was dried and the 3-phenylpyrazoline isolated by distillation in a stream of nitrogen. The yield was 8.3 g (28%), b.p. 146-148° at 9 mm, m.p. 44-45°. The N-nitroso derivative had m.p. 155°; the melting point was not depressed by admixture with 1-nitroso-3-phenylpyrazoline, prepared by the previous method.

3-p-Tolylpyrazoline. a) This was prepared from 34 g of β-dimethylamino-p-methylpropiophenone hydrochloride similarly to 3-phenylpyrazoline (experiment "a"), but it was isolated after distilling off the solvent in vacuum in a stream of nitrogen without heating, as a thick crystalline mass.[*] The yield was 17.4 g (72.6%), m.p. 76-78°, N-nitroso derivative m.p. 130° (from alcohol). The constants agreed with those described previously [3].

b) It was prepared from 26.8 g of p-methylacetophenone similarly to 3-phenylpyrazoline (experiment "b"), but was isolated by the method described above. The yield was 23 g (71.8%).

3-p-Methoxyphenylpyrazoline. a) This was prepared from 36.4 g of β-dimethylamino-p-methoxypropiophenone hydrochloride similarly to 3-p-tolylpyrazoline (experiment "a"). The yield was 16.9 g (68%), m. p. 93-96°, N-nitroso derivative m.p. 169° (from alcohol). The constants agree with those described previously [3].

b) It was prepared from 30 g of p-methoxyacetophenone similarly to 3-p-tolylpyrazoline (experiment "b"), yield 19.5 g (55.3%).

3-(2,5-Dimethylphenyl)-pyrazoline. a) This was prepared from 24.1 g of β-dimethylamino-2,5-dimethylpropiophenone hydrochloride similarly to 3-phenylpyrazoline (experiment "a"). The yield was 10.5 g (61.1%).

B.p. 145-146° at 5 mm, n_D^{20} 1.5943; d_4^{20} 1.0658, MR$_D$ 55.55; calc. 53.07, EM$_D$ 2.48.[**]

The N-nitroso derivative had m.p. 112°. The constants agree with the values given previously [2].

b) It was prepared from 29.6 g of 2,5-dimethylacetophenone similarly to 3-phenylpyrazoline (experiment "b"). The yield was 21.5 g (61.7%).

c) It was prepared from 29.6 g of 2,5-dimethylacetophenone similarly to 3-phenylpyrazoline (experiment "c"). The yield was 5.3 g (15.1%), b.p. 142-143° at 4 mm, n_D^{20} 1.5948. The N-nitroso derivative had m.p. 112°, undepressed by admixture with 1-nitroso-3-(2,5-dimethylphenyl)-pyrazoline, prepared by the previous method.

3-Phenyl-4-ethylpyrazoline. This was prepared from 29.6 g of butyrophenone, paraformaldehyde and hydrazine hydrochloride similarly to 3-phenylpyrazoline (experiment "c"). The yield was 1.5 g, b.p. 129° at 5 mm. The N-nitroso derivative had m.p. 81° (from ether), undepressed by admixture with 1-nitroso-3-phenyl-4-ethylpyrazoline, prepared from α-dimethylaminomethylbutyrophenone [2].

SUMMARY

1. A new method of synthesizing the pyrazoline ring by reacting alkylaryl ketones with paraformaldehyde and hydrazine is described.

2. The effect of substituents on the yield of 3-arylpyrazolines from β-dialkylaminopropiophenones was investigated.

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[*] If the methyl alcohol was distilled off with heating, then the 3-p-tolylpyrazoline was obtained as a difficultly crystallizable oil.

[**] According to Auwers' data [6], EM$_D$ for various 3-phenylpyrazolines approximately equals + 2. The refraction for -N-N= was taken as 5.781 [7].

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INVESTIGATION OF FURAN COMPOUNDS

VIII. SELECTIVE HYDROGENATION OF THE ETHYLENIC BOND OF α,β-UNSATURATED FURAN ALDEHYDES AND KETONES IN THE PRESENCE OF RANEY NICKEL

A. A. Ponomarev and Z. V. Til

The reduction of α,β-unsaturated ketones is one of the general methods of preparing saturated ketones. For this purpose, both nascent hydrogen and catalytic promotion are used. The synthesis of saturated furan ketones is carried out in this way in a series of cases. Kasiwagi [1] and Harries [2], using sodium amalgam, reduced several furfurylidene ketones to saturated ones. Platinum, palladium and nickel catalysts have been used for hydrogenation in the liquid phase at room temperature. Using various platinum catalysts, some saturated furan ketones [3, 4] were prepared from monounsaturated ones. We showed [5-7] that by using Adam's platinum catalyst and palladium on animal charcoal, the reaction could be stopped at the stage of the formation of saturated ketone not only in the case of monounsaturated ones but also diene and triene furan ketones.

Wienhaus and Leonhardi [8] prepared furylpropionaldehyde and furylhexanone-5 from furylacrolein and furylhexadienone with reduced nickel in an alcohol solution. Raney nickel (treated with CO_2) was used for hydrogenation, under the usual conditions, of difurfurylideneacetone to difurfurylacetone [9]. Burdick and Adkins [10] reduced furylacrolein to furylpropionaldehyde at 23° under pressure in the presence of Raney nickel; besides the aldehyde, a large amount of furylpropanol was formed and some furylacrolein remained unreacted. It was reported recently [11] that 75% of difurfurylideneacetone was converted into difurfurylacetone by hydrogenating with Raney nickel with the addition of a small amount of methyl iodide. It is also known that furfurylideneacetofuran was hydrogenated to furfurylacetofuran in the presence of nickel on celite at 45-66° under a pressure close to 100 atm.[12].

The main disadvantage of the method of preparing saturated furan ketones from unsaturated ones by hydrogenating them at room temperature and normal pressure in the presence of a catalyst of the platinum group, is, besides the cost of catalyst, the length of the operation and the necessity of working with relatively small amounts of material. As can be seen from the data given below, the hydrogenation of furfurylidenemethyl isohexyl ketone in the presence of Raney nickel under similar conditions also proceeds slowly.

Our experiments showed, however, that α,β-unsaturated furan aldehydes and ketones may be converted into the corresponding saturated ones rapidly and in good yields by hydrogenation with Raney nickel at room temperature and under pressure(20 atm. and above) and with the introduction into the autoclave of the calculated amount of hydrogen required to saturate the ethylenic bonds. Anhydrous alcohol, in a volume not less than that of the material, was used as solvent. The amount of Raney nickel introduced was from 5 to 10% of the weight of the unsaturated compound. Usually 1-2 hours were required to hydrogenate 100-200 g of material. This method was tested by the hydrogenation of furylacrolein, furfurylideneacetone, furfurylidenemethyl ethyl ketone, furfurylidenemethyl isobutyl ketone, furfurylideneacetophenone and 1-(α-furyl)-hexadien-1,3-one-5. The yields of saturated furan aldehydes and ketones thus obtained and their properties are given in the table.

EXPERIMENTAL *

Furylacrolein and furfurylideneacetone were prepared by the usual method [17, 18]. Furfurylidenemethyl ethyl ketone, furfurylideneacetophenone and furylhexadienone were prepared according to the data in [6, 13].

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* K. Sapunar, G. Evseeva and L. Khomyakova helped with some of the syntheses.

Furfurylidenemethyl isobutyl ketone was prepared by condensing furfurol with methyl isobutyl ketone in an alcohol-water medium in the presence of sodium hydroxide; the liquid had b.p. 119-121° (6.5 mm), n_D^{20} 1.5520; the semicarbazone had m.p. 174-175°; literature data [8]: b.p. 115-116° (3 mm), n_D^{20} 1.5528; semicarbazone m.p. 175-176°. Raney nickel was prepared by the usual method[6].

Formula of aldehyde or ketone	Yield (in %)	Boiling point	n_D^{20}	d_4^{20}	Melting point of derivative
$-CH_2-CH_2-CHO$*	52	81–82° (17mm)	1.4766	—	See [13]
$-CH_2-CH_2-CO-CH_3$**	80–87	94–96 (15mm)	1.4710	1.0323	Semicarbazone, m.p. 141-142°
$-CH_2-CH_2CO-C_2H_5$***	72–75	88–89 (10mm)	1.4698	1.0105	—
$-CH_2-CH_2-CO-CH_2CH(CH_3)_2$	76–85	111–112 (9mm)	1.4630	0.9706	—
$-(CH_2)_4-CO-CH_3$****	72	94–96 (2mm)	1.4705	—	Semicarbazone, m.p. 119-120°
$-CH_2-CH_2-CO-C_6H_5$	81	161–163 (8.5mm); m.p. 40°	—	—	—

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* Literature data: B. p. 81° (17 mm), n_D^{19} 1.4772, d_4^{19} 1.0574 [14]; b. p. 80-85° (15 mm), n_D^{20} 1.4771 [15].

** Literature data: b.p. 95° (15 mm), n_D^{25} 1.4697, d_4^{25} 1.0258 [16]; b.p. 95° (15 mm), d^{19} 1.0361 [2]; b.p. 81° (10 mm), n_D^{25} 1.470, n_4^{25} 1.026 [1].

*** Literature data: b. p. 88.5° (10 mm), n_D^{25} 1.4670, d_4^{25} 1.0029 [16]; b.p. 88° (10 mm), n_D^{25} 1.4680, d_4^{25} 1.003 [1].

**** Literature data: b.p. 93-95° (2 mm), n_D^{20} 1.47023, d^{20} 0.995; semicarbazone: m.p. 121-122° [8].

Hydrogenation was carried out in rotating steel autoclaves of 0.5 and 0.15 liters capacity. The calculated amount of hydrogen was introduced into the autoclave and hydrogenation was complete when the pressure fell to zero.

1-(α-Furyl)-5-methylhexanone-3. 20 g of furfurylidenemethyl isobutyl ketone, dissolved in 75 ml of anhydrous alcohol, and 2.5 g of Raney nickel were placed in a rotating autoclave of 0.15 liters capacity and a pressure of 60 atm. of hydrogen introduced into the autoclave. Hydrogenation of one of the double bonds of the sample taken required 2800 ml of hydrogen, which corresponded to the amount of hydrogen introduced into the autoclave. Hydrogenation was complete in 1 hour. After distilling off the solvent, the hydrogenation product was distilled in vacuum. We obtained a fraction with b.p. 111-112° (9 mm) (15.35 g). The liquid had a pleasant smell:

n_D^{20} 1.4630, d_4^{20} 0.9706, MR_D 51.15; calc. 51.52. The ketone did not form a semicarbazone or an oxime.

Found %: C 72.65; H 9.16; OH (by Terentyev's method)– none. $C_{11}H_{16}O_2$. Calculated %: C 73.30; H 8.95; OH 0.0.

1-(α-Furyl)-3-phenylpropanone-3. 18 g of furfurylideneacetophenone, 30 ml of anhydrous alcohol and 2 g of Raney nickel were loaded into an autoclave of 0.15 liters capacity, into which hydrogen was then compressed (24 atm.). After 2 hours 2400 ml of hydrogen had been absorbed; the calculated amount for one double bond was 2270 ml. After removing the catalyst and alcohol, the residue was distilled in vacuum. We obtained a fraction with b.p. 161-163° (8.5 mm). To prevent the substance from crystallizing out in the condenser, the latter was filled with hot water. The yield was 14.8 g (81.4%). The liquid quickly crystallized in the receiver, changing into slightly yellowish, needle-like crystals with m.p. 40°.

Found %: 78.22, 78.16; H 6.27, 6.3; OH – none. M 201.9. $C_{13}H_{12}O_2$. Calculated %: C 77.97; H 6.03; OH 0.0. M 200.2.

The ketone was soluble in ether, benzene and alcohol and insoluble in water.

1-(α-Furyl)-7-methyloctanone-3. 10 g of furfurylidenemethyl isohexyl ketone, 40 ml of anhydrous alcohol and 1 g of Raney nickel were loaded into a rocking flask for hydrogenation. Hydrogenation was stopped after 10 hours, when 1310 ml of hydrogen had been absorbed (1250 ml of hydrogen was the calculated amount for one double bond). The catalyst was filtered off from the catalyzate, the alcohol distilled off and the residue was distilled in vacuum. We obtained a fraction with b.p. 117-118° (1.5 mm); yield 7.7 g (76.26%). The slightly yellowish liquid had a pleasant flower-like smell. The ketone was soluble in alcohol, ether and benzene; insoluble in water:

n_D^{20} 1.6338, d_4^{20} 0.9532, MR_D 60.28; calc. 60.75.

Found %: C 75.12; H 9.59; OH – none. M 207.7, 207.9. $C_{13}H_{20}O_2$. Calculated %: C 74.95; H 9.67; OH 0.0. M 208.3.

The ketone did not form derivatives with semicarbazide or 2,4-dinitrophenylhydrazine.

SUMMARY

1. By hydrogenation of α,β-unsaturated furan aldehydes and ketones at room temperature under pressure in the presence of Raney nickel the corresponding saturated furan aldehydes and ketones were formed in good yields.

2. The properties of 1-(α-furyl)-5-methylhexanone-3, 1-(α-furyl)-3-phenylpropanone-3 and 1-(α-furyl)-7-methyloctanone-3 formed were described for the first time.

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THE SYNTHESIS AND PROPERTIES OF METHYLPHENYLCARBINOL DERIVATIVES

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In connection with the synthesis of p-nitroacetophenone, we investigated the possibility of direct nitration of methylphenylcarbinol and hydrolysis of the nitrate of p-nitrophenylmethylcarbinol. p-Nitrophenylmethylcarbinol has been prepared previously [1] by hydrolyzing the nitration product of the acetate of methylphenylcarbinol. The direct nitration of methylphenylcarbinol has not been investigated. The above authors also prepared the nitrate of p-nitrophenylmethylcarbinol by nitration of α-chloroethylbenzene, however, it was not hydrolyzed. According to data [2], hydrolysis leads only to tarry products, and the carbinol was obtained from the nitrate only through intermediate conversion into the acetate.

We carried out the nitration of methylphenylcarbinol, as well as its methyl and ethyl ethers. It was found that in all cases, the nitrates of o- and p-nitrophenylmethylcarbinols were formed in approximately equal amounts. The nitration proceeded smoothly and with satisfactory yield, when the nitric acid was free from nitrogen oxides and nitrous acid. It was established that, contrary to data [2], the nitrate esters are hydrolyzed smoothly by water in a neutral medium.

The facility with which α-ester groups of various methylphenylcarbinol derivatives split off depends on the character of the substituent at the β-carbon atom. The nitrate of p-nitrophenylmethylcarbinol is readily hydrolyzed; the nitrate of p-nitrophenylbromomethylcarbinol is hydrolyzed with much greater difficulty [2]. Analogously, the alkoxy group is readily substituted in the nitration of methyl or ethyl ethers of methylphenylcarbinol while the alkoxy group is not exchanged in the nitration of the corresponding ethers of phenylchloromethylcarbinol [3].

EXPERIMENTAL

Nitration of methylphenylcarbinol. A current of carbon dioxide was passed through nitric acid (70 ml, d 1.5) heated to 50° and 4 g of urea was added. 0.2 g of sulfanilic acid was added to the nitric acid thus freed from oxides of nitrogen and then 20 g of methylphenylcarbinol was added dropwise at –5°. After pouring onto ice and filtering, we obtained 18 g of the crude nitrate of p-nitrophenylmethylcarbinol [after recrystallization from methanol, 13.9 g (40%); m.p. 50-51°] and 16.8 g of a liquid product, containing mainly the nitrates of o- and p-nitrophenylmethylcarbinol. The nitrate of p-nitrophenylmethylcarbinol was quite stable and distilled at 130-133° (0.3 mm).

Ethers of methylphenylcarbinol were prepared by adding 12.5 ml of concentrated sulfuric acid to a mixture of 25 ml of methylphenylcarbinol and 50 ml of the appropriate alcohol, while cooling in ice, and subsequently heating at 55° for 2 hours; the yield of the methyl ether was 80.5%, n_D^{20} 1.493, b. p. 70-72° (21 mm); the yield of ethyl ether was 78%, n_D^{20} 1.487, b. p. 70-72° (10 mm); the yield of isopropyl ether was 35%, n_D^{20} 1.486, b.p. 82-84° (19 mm). In all the cases, the di-α-phenethyl ether was formed in up to 5% yield, n_D^{20} 1.539, d_4^{20} 1.000, b.p. 103-105° (0.3 mm).

The nitration of the ethers of methylphenylcarbinol was carried out under the same conditions as in the nitration of methylphenylcarbinol. The yield of the nitrate of p-nitrophenylmethylcarbinol was 35% in the case of the methyl ether and 30% in the case of the ethyl.

p-Nitrophenylmethylcarbinol was prepared by hydrolyzing the nitrate with a 3% aqueous solution of urea at 100° for 8 hours. After oxidizing the p-nitrophenylmethylcarbinol with chromium trioxide [1], p-nitroacetophenone was formed in 88% yield, calculated on the nitrate. The mixture of isomers formed in the nitration was also hydrolyzed and oxidized to a mixture of isomers of nitroacetophenone, from which p-nitroacetophenone was crystallized out. After recrystallization from methanol, the yield of the latter (m.p. 79-80°) was 40%, calculated on methylphenylcarbinol.

SUMMARY

1. Direct nitration of methylphenylcarbinol gives nitrates of o- and p-nitrophenylmethylcarbinols, which are relatively easily hydrolyzed by water.

2. Methylphenylcarbinol ethers split off the ether group more readily than the corresponding ethers of styrene halohydrins.

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PHOSPHATE ESTERS OF TRICHLORIMINOACETIC ACID AND ESTERS OF TRIOXYPHOSPHAZOTRICHLOROACETYL. II

A. V. Kirsanov and G. I. Derkach

Esters of the type $CCl_3CON = P(OR)_3$ and $CCl_3(OR) = NPO(OR)_2$ are thick, viscous liquids, that will not distil without decomposition, which makes their purification and identification extremely difficult [1]. The α-naphthyl and 4-chloro-1-naphthyl esters that we prepared were crystalline materials. We were able to find the reaction schemes for α-naphthyl esters which fully prove their structure and confirm the conclusions in report [1].

$$\begin{tikzcd}
CCl_3CON{=}PCl_3 \arrow[r, "+\,3\alpha\text{-}C_{10}H_7ONa"] \arrow[d, "+\,H_2O"] & CCl_3CON{=}P(OC_{10}H_7\text{-}\alpha)_3 \arrow[d, "+\,NaOH"] \\
CCl_3CONHPOCl_2 \arrow[r, "+\,2\alpha\text{-}C_{10}H_7ONa"] \arrow[d, shift right, "+\,PCl_5"'] & CCl_3CONHPO(OC_{10}H_7\text{-}\alpha)_2 \\
CCl_3CCl{=}NPOCl_2 \arrow[r, "+\,3\alpha\text{-}C_{10}H_7ONa"] \arrow[u, shift right, "+\,H_2O"'] & CCl_3(OC_{10}H_7\text{-}\alpha){=}NPO(OC_{10}H_7\text{-}\alpha)_2 \arrow[u, "+\,NaOH"]
\end{tikzcd}$$

Tri-α-naphthoxyphosphazotrichloroacetyl is considerably more stable to hydrolysis than liquid triphenoxyphosphazotrichloroacetyl [1]. It can be readily recrystallized and shows a sharp melting point over a range of two degrees. The isomeric, tri-α-naphthyl N-phosphate of trichloriminoacetic acid is a solid glass-like material with a quite definite, though not very sharp (over a range of four degrees) melting point; it will not recrystallize. Tri-α-(4-chloronaphthoxy)-phosphazotrichloroacetyl is hydrolyzed with greater difficulty than the triphenyl derivative, but with noticeably greater facility than tri-α-naphthoxyphosphazotrichloroacetyl.

EXPERIMENTAL

Tri-α-naphthoxyphosphazotrichloroacetyl. 0.045 g at. of sodium was dissolved in a solution of 0.045 mole of α-naphthol in 70 ml of ether. When the sodium had completely dissolved, a solution of 0.015 mole of trichlorophosphazotrichloroacetyl in 50 ml of ether was slowly added with stirring. The reaction proceeded with the evolution of heat. After all the chloride had been added, stirring was continued for a further 15-20 minutes. Then the mixture was heated to boiling and the sodium chloride filtered off. On cooling, the triether separated out from the solution as fine, transparent prisms. Part of the triether remained with the sodium chloride and could be extracted with boiling ether. For purification, the substance was recrystallized from petroleum ether. The total yield was 7.2 g (77.5%), m.p. 114-116°. Tri-α-naphthoxyphosphazotrichloroacetyl is readily soluble in benzene and difficultly soluble in carbon tetrachloride, petroleum ether, alcohol and ether. On boiling with water it hydrolyzes very slowly, but readily splits out one phenoxyl group on heating with a solution of alkali in aqueous alcohol.

Found %: N 2.23. $C_{32}H_{21}O_4NPCl_3$. Calculated %: N 2.25.

The tri-α-naphthyl N-phosphate of trichloriminoacetic acid. A solution of 0.02 mole of the acid chloride of trichloriminoacetyl chloride N-phosphoric acid in 50 ml of ether was slowly added to a solution of 0.06 mole of sodium α-naphtholate in 60 ml of ether with stirring and cooling in ice-water. The reaction proceeded violently and was complete in 10-15 minutes. The reaction mixture was cooled to 0°, quickly washed with 70 ml of 1 N sodium hydroxide solution with ice and the ether layer separated and filtered successively through two funnels, arranged one above the other, with filters containing 5.0 g of anhydrous sodium sulfate. The clear ether solution was immediately evaporated in vacuum, initially at 10-15° and finally at 50°. There remained the tri-α-naphthyl N-phosphate of trichloriminoacetic acid as an almost colorless, transparent, friable, glassy mass, which was easily powdered, m.p. 60-64°. The yield was 4.6 g (37.1%).

Found %: N 2.32. $C_{32}H_{21}O_4NPCl_3$. Calculated %: N 2.25.

The di-α-naphthyl ester of N-trichloroacetylamidophosphoric acid. A solution of 0.02 mole of the acid chloride of N-trichloroacetylamidophosphoric acid in 40 ml of ether was added with stirring over a period of 10-15 minutes to a solution of 0.04 mole of sodium α-naphtholate in 45 ml of ether, and then the mixture was boiled under reflux for 10 minutes. The precipitated sodium chloride was filtered off and the ether solution evaporated in vacuum, finally at 60-70°. An oily liquid remained, which readily crystallized on cooling and rubbing with a glass rod. The solid product was filtered off in vacuum, washed with alcohol (twice with 3 ml) and recrystallized from alcohol. The di-α-naphthyl ester of N-trichloroacetylamidophosphoric acid formed colorless prisms (m.p. 139-141°); it was readily soluble in acetone and ether, more difficultly in carbon tetrachloride, alcohol and benzene and insoluble in water. The yield was 6.6 g (66.8%). It was hydrolyzed with considerably more difficulty than the corresponding phenyl ester and titrated against alkali as a monobasic acid.

Found %: N 2.33; equiv. 1.003. $C_{22}H_{15}O_4NPCl_3$. Calculated %: N 2.48; equiv. 1.000.

Hydrolysis of tri-α-naphthoxytrichloroacetyl. A mixture of 0.001 mole of the triether, 30 ml of alcohol and 2 ml of 1 N sodium hydroxide solution was boiled under reflux until the triether dissolved (50-60 minutes), the alcohol was distilled off in vacuum and 5 ml of water and 3 ml of 1 N hydrochloric acid solution were added to the residue. On cooling, the di-α-naphthyl ester of N-trichloroacetylamidophosphoric acid precipitated from the solution, was filtered off in vacuum, washed with water (twice with 1 ml) and alcohol (1 ml) and recrystallized from alcohol. The yield was 0.3 g (60.9%), m.p. 139-141°; the melting point was not depressed by admixture with a sample of the diester, prepared from the dichloride.

Hydrolysis of the tri-α-naphthyl N-phosphate of trichloriminoacetic acid. On hydrolyzing with water, the yield of the di-α-naphthyl ester of N-trichloroacetylamidophosphoric acid was very low as many tarry products were formed. Therefore the hydrolysis was performed with alkali under the same conditions as for tri-α-naphthoxytrichloroacetyl. After distilling off the alcohol in vacuum, a green aqueous solution remained, from which the diester was precipitated together with tarry substances on acidifying. To remove the latter, the precipitate was filtered in vacuum, carefully washed with ether (6 times with 0.5 ml) and then alcohol and recrystallized from alcohol. The yield was 0.25 g (36.3%), m.p. 139-141°; it was identified by a mixed melting point with authentic di-α-naphthyl ester of N-trichloroacetylamidophosphoric acid.

(I) $CCl_3CON{=}P(\alpha\text{-}C_{10}H_6Cl\text{-}4)_3$
(II) $CCl_3C[{=}NPO(\alpha\text{-}OC_{10}H_6Cl\text{-}4)_2](\alpha\text{-}OC_{10}H_6Cl\text{-}4)$
(III) $CCl_3CONHPO(\alpha\text{-}OC_{10}H_6Cl\text{-}4)_2$

Tri-α-(4-chloronaphthoxy)-phosphazotrichloroacetyl (I). Sodium 4-chloronaphtholate was prepared from 1,4-chloronaphthol and an alcohol solution of sodium ethylate with subsequent distillation of the alcohol in vacuum. The reaction was immediately carried out in the same flask. A solution of 0.01 mole of trichlorophosphazotrichloroacetyl in 45 ml of ether was slowly added with stirring to 0.03 mole of 4-chloronaphtholate (15-20 minutes). Then the reaction mixture was heated to boiling and filtered. On cooling, tri-α-(4-chloronaphthoxy)-phosphazotrichloroacetyl crystallized out from the filtrate. To isolate the substance remaining in solution, the ether was distilled off in vacuum. After recrystallization from petroleum ether, the tri-α-(4-chloronaphthoxy)-phosphazotrichloroacetyl appeared as fine colorless prisms (m.p. 124-125°); readily soluble in acetone and more difficultly in carbon tetrachloride, ether and benzene. The yield was 3.6 g (49.8%).

Found %: N 2.01. $C_{32}H_{18}O_4NPCl_6$. Calculated %: N 1.93.

All operations in the preparation of tri-α-(4-chloronaphthoxy)-phosphazotrichloroacetyl must be carried out as quickly as possible; solutions should be protected from moisture in the air, as the triester is very readily hydrolyzed. Therefore, together with the triester, one usually obtains a quite significant amount (about 2 g) of the di-α-4-chloronaphthyl ester of N-trichloroacetylamidophosphoric acid with m.p. 180-182°.

The tri-α-(4-chloronaphthyl) N-phosphate of trichloriminoacetic acid (II). A solution of 0.01 mole of the acid chloride of trichloriminoacetyl chloride N-phosphoric acid in 40 ml of ether was added over a period of 10-15 minutes to 0.03 mole of 4-chloronaphtholate with stirring and cooling in ice-water. The reaction mixture was then washed with 40 ml of 1 N sodium hydroxide solution with ice, the water layer quickly separated and the ether solution immediately passed through two funnels, arranged one above the other, containing 5.0 g of finely powdered, anhydrous sodium sulfate. The clear ether solution was immediately evaporated in vacuum: initially at 10-15° and finally at 50°. There remained the tri-α-(4-chloronaphthyl) N-phosphate of trichloriminoacetic acid as a waxy, almost colorless substance. The yield was 4.5 g (62.1%), m.p. 36-45°.

Found %: N 1.87. $C_{32}H_{18}O_4NPCl_4$. Calculated %: N 1.93.

The substance was very easily hydrolyzed to the diester by moisture in the air.

Hydrolysis of tri-α-(4-chloronaphthoxy)-phosphazotrichloroacetyl. 0.001 mole of the triester was boiled under reflux with 10 ml of ethyl alcohol (96%) until it dissolved (about 5 minutes). On cooling, large prisms of the di-α-(4-chloronaphthyl) ester of trichloroacetylamidophosphoric acid (III) crystallized out from the solution; m.p. 180-182°. The yield was 0.4 g (71.0%). The substance was readily soluble in ether, benzene and carbon tetrachloride and difficultly soluble in alcohol and petroleum ether. It dissolved in aqueous solutions of alkaline hydroxides and carbonates to form salts.

Found %: N 2.50; equiv. 1.040. $C_{22}H_{13}O_4NPCl_5$. Calculated %: N 2.48; equiv. 1.000.

Hydrolysis of the tri-α-(4-chloronaphthyl) N-phosphate of trichloriminoacetic acid. 0.001 mole of the substance was mixed with 10 ml of alcohol and heated. The substance dissolved at 30-40° in a few minutes. On cooling, the di-α-(4-chloronaphthyl) ester of trichloroacetylamidophosphoric acid separated, m.p. 180-182°. The yield was 0.42 g (74.5%); the melting point was undepressed by admixture with a sample of the diester, prepared by hydrolysis of tri-α-(4-chloronaphthoxy)-phosphazotrichloroacetyl.

SUMMARY

Crystalline tri-α-naphthoxy- and tri-α-(4-chloronaphthoxy)-phosphazotrichloroacetyls and the isomeric α-naphthyl and α-(4-chloronaphthyl) N-phosphates of trichloriminoacetic acid, were prepared and their properties described.

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THE SYNTHESIS OF SOME ISOTHIOUREA AND CYSTINEAMINE DERIVATIVES

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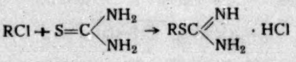
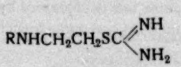
Some isothiourea and cystineamine derivatives were synthesized for pharmacological investigations of sulfur-containing compounds. Various methods are described in the literature for preparing isothiuronium compounds [1-5]. The most convenient method of synthesis is by reacting chlorides or bromides of suitable compounds in an alcoholic medium [2, 4, 5].



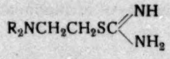
$$RCl + S{=}C\begin{matrix}NH_2\\NH_2\end{matrix} \rightarrow RSC\begin{matrix}NH\\NH_2\end{matrix}\cdot HCl$$

We synthesized isothiuroniums, which are derivatives of ethanolamine and thiourea, of the general formula



$$RNHCH_2CH_2SC\begin{matrix}NH\\NH_2\end{matrix}$$

(R-butyl, phenylethyl, benzyl), as well as disubstituted derivatives



$$R_2NCH_2CH_2SC\begin{matrix}NH\\NH_2\end{matrix}$$

(R-dibenzyl, phenyl and methyl). The compounds mentioned are not described in the literature.

Besides the isothiuronium compounds, the same derivatives of cystineamine-diaminodiethyldisulfide were synthesized and these were obtained by heating suitable chlorides with sodium disulfide in an aqueous solution[6].

$$2RCl + Na_2S_2 \rightarrow RSSR + 2NaCl$$

This method is outstanding in simplicity and convenience. The disulfide bases obtained in this way were extracted from the aqueous solution with ether and then precipitated as hydrochlorides.

EXPERIMENTAL

Butylaminoethylisothiuronium. 1 mole of butylaminoethyl chloride hydrochloride (m.p. 218-220°) and 1.1 moles of thiourea were boiled in anhydrous alcohol for 12 hours. The precipitated butylaminoethylisothiuronium hydrochloride was purified by recrystallization from butyl and then ethyl alcohol. All the subsequent thiuroniums were prepared by a similar method; they were white crystalline products with definite melting points. The starting aminoethanols and their chlorides were prepared by methods described in the literature [7-12] (Table 1).

Dibutylcystineamine hydrochloride was prepared by boiling a mixture of 1 mole of butylaminoethyl chloride hydrochloride and 2 moles of sodium disulfide in water for 2 hours. The oily product, which separated from the aqueous solution, was extracted with ether and precipitated from the dry ether solution with hydrogen chloride.

TABLE 1

Properties and Analyses of the Isothiuronium Compounds Prepared

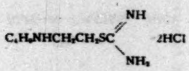
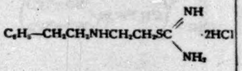
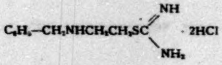
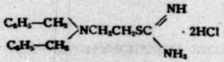
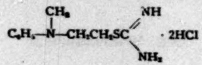
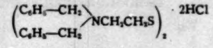
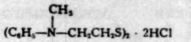
Name of compound	Formulae of compounds	Melting point	Solubility	Analysis results				
				found (%)		formula	calculated (%)	
				C	H		C	H
Butylaminoethylisothiuronium (hydrochloride)	 $C_4H_9NHCH_2CH_2SC(=NH)NH_2 \cdot 2HCl$	169—170°	Water, hot alcohol; insoluble in ether and benzene	33.56	7.32	$C_7H_{19}N_3SCl_2$	33.8	7.6
β-Phenylethylaminoethylisothiuronium (hydrochloride)	 $C_6H_5{-}CH_2CH_2NHCH_2CH_2SC(=NH)NH_2 \cdot 2HCl$	174—175	Water, hot alcohol; insoluble in ether and benzene	45.02	6.51	$C_{11}H_{19}N_3SCl_2$	44.6	6.4
Benzylaminoethylisothiuronium (hydrochloride)	 $C_6H_5{-}CH_2NHCH_2CH_2SC(=NH)NH_2 \cdot 2HCl$	138—140	Water, hot alcohol; insoluble in ether	42.84	5.94	$C_{10}H_{17}N_3SCl_2$	42.5	6.0
Dibenzylaminoethylisothiuronium (hydrochloride)	 $(C_6H_5{-}CH_2)_2NCH_2CH_2SC(=NH)NH_2 \cdot 2HCl$	178—180	Water, hot alcohol; insoluble in ether and benzene	54.58	6.49	$C_{17}H_{23}N_3SCl_2$	54.84	6.2
N,N-phenylmethylaminoethylisothiuronium (hydrochloride).	 $C_6H_5{-}N(CH_3){-}CH_2CH_2SC(=NH)NH_2 \cdot 2HCl$	144—145	Water, hot alcohol; insoluble in benzene, ether and acetone	42.57	6.40	$C_{10}H_{17}N_3SCl_2$	42.5	6.0

TABLE 2

Properties and Analyses of the Cystineamine Derivatives Prepared

Name of compound	Formulae of compounds	Melting point	Solubility	Analysis results				
				found (%)		formula	calculated (%)	
				C	H		C	H
Dibutylcystineamine (hydrochloride)	$(C_4H_9NHCH_2CH_2S)_2 \cdot 2HCl$	260—261°	Water, hot alcohol; insoluble in ether	43.10	8.42	$C_{12}H_{30}N_2S_2Cl_2$	42.7	8.8
Di-(β-phenylethyl)-cystineamine (hydrochloride)	$(C_6H_5{-}CH_2CH_2NHCH_2CH_2S)_2 \cdot 2HCl$	249—250	Hot water and alcohol; difficultly soluble in cold water; insoluble in benzene and ether	55.62	6.80	$C_{20}H_{30}N_2S_2Cl_2$	55.42	6.9
Dibenzylcystineamine (hydrochloride)	$(C_6H_5{-}CH_2NHCH_2CH_2S)_2 \cdot 2HCl$	234—235	Hot water and alcohol; insoluble in cold water, benzene, ether and acetone	53.21	5.82	$C_{18}H_{26}N_2S_2Cl_2$	53.58	6.4
Tetrabenzylcystineamine (hydrochloride)	 $\left({C_6H_5{-}CH_2 \atop C_6H_5{-}CH_2} \right\rangle NCH_2CH_2S \Big)_2 \cdot 2HCl$	168—170	Water, hot alcohol; insoluble in benzene	65.41	6.49	$C_{32}H_{38}N_2S_2Cl_2$	65.6	6.5
Diphenyldimethylcystineamine (hydrochloride)	 $(C_6H_5{-}\overset{CH_3}{\overset{\vert}{N}}{-}CH_2CH_2S)_2 \cdot 2HCl$	164—165	Hot ethyl and butyl alcohol; insoluble in benzene and hydrolyses in water	53.49	6.52	$C_{18}H_{26}N_2S_2Cl_2$	53.58	6.4

The other derivatives of cystineamine were prepared by a similar method; they were white crystalline products, with definite melting points (Table 2).

SUMMARY

Butylaminoethylisothiuronium, benzylaminoethylisothiuronium, dibenzylaminoethylisothiuronium, phenylethylaminoethylisothiuronium and diphenylmethylaminoethylisothiuronium hydrochlorides, which have not been described in the literature, were synthesized from butylaminoethylchloride, benzylaminoethylchloride, dibenzylaminoethylchloride, phenylethylaminoethylchloride and phenylmethylaminoethylchloride hydrochlorides and thiourea and their properties described. N,N'-Dibutylcystineamine, N,N'-dibenzylcystineamine, N,N'-tetrabenzylcystineamine, N,N'-(β-phenylethyl)-cystineamine and N,N'-diphenyldimethylcystineamine hydrochlorides, which have not been described in the literature, were synthesized from the same chlorides and sodium disulfide and their properties described.

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INVESTIGATION IN THE FIELD OF QUINONES

XVI. SYNTHESIS OF SUBSTITUTED BENZOFURANS

A. N. Grinev, Pan Bon Khvar and A. P. Terentyev

In a previous paper, we showed that condensation of p-benzoquinone with ethyl acetoacetate with gradual addition of quinone to the reaction liquid gave mainly ethyl 2-methyl-5-hydroxybenzofuran-3-carboxylate in a yield higher than 67% [1]. However, besides the latter, diethyl 2,6-dimethylbenzo-(1,2-b; 4,5-b')-difuran-3,7-dicarboxylate was also formed. The separation of these compounds is somewhat difficult, while the reaction itself requires much time and attention. By using an extractor without a syphon [2] as the reactor, we have now succeeded in preparing ethyl 2-methyl-5-hydroxybenzofuran-3-carboxylate (I) with no impurities in a yield close to quantitative, as well as simplifying the method of condensation. Some reactions of the ester (I) have also been investigated in this work. Acid (II), prepared by the hydrolysis of (I), described previously [1], was readily converted into 2-methyl-5-hydroxybenzofuran (III) by heating with calcium oxide. The phenolic characteristics of (III), in contrast to ester (I), are clearly expressed: 2-methyl-5-hydroxybenzofuran (III) reacts with ferric chloride to give a complex compound with p-benzoquinone, and undergoes other reactions characteristic of phenols. The structure of (III) was proved since methylation of the compound gave 2-methyl-5-methoxybenzofuran (IV), characterized in one of our reports [1].

EXPERIMENTAL

1. Ethyl 2-methyl-5-hydroxybenzofuran-3-carboxylate (I). A solution of 35 g of zinc chloride in 40 ml of anhydrous alcohol, 65 g of ethyl acetoacetate and 50 ml of absolute ether were mixed in the flask of an extractor. 27 g of p-benzoquinone was placed in the thimble of the extractor. The flask of the extractor was heated for 27 hours at 110-120°* (thermometer in the air bath). The extractor discharged at 30 drops a minute. The reaction liquid was cooled and the precipitated crystals separated and washed with a small amount of benzene. We obtained 31 g of (I). After gradual evaporation of the ether, we obtained a further 14 g of (I) from the mother liquor. The mother liquor remaining after the separation of the crystals was treated several times with water. The polycrystalline mass formed dissolved in the ether and the ether solution was dried with calcium chloride. The ether was evaporated off. The crystals formed were filtered off and washed with benzene. We obtained 9 g of crystals of (I). The total yield was 54 g (98%). The m.p. of 137° (from alcohol) agreed with literature data [3].

2. Ethyl 2-methyl-5-benzoxybenzofuran-3-carboxylate (V). 2.2 g of (I) was dissolved in 3 ml of pyridine. On cooling, 1.1 ml of benzoyl chloride was added. The reaction mixture was kept at room temperature for 4 hours and treated with 10% sulfuric acid. The crystals of (V) formed were washed with water and dried. The yield was 2.5 g. The m.p. was 102° (from alcohol).

Found %: C 70.42, 70.53; H 5.17, 4.81. $C_{19}H_{16}O_5$. Calculated %: C 70.36; H 4.97.

3. 2-Methyl-5-hydroxybenzofuran (III). A tube filled with a mixture of 37 g of the acid (II) and 33.6 g of calcium oxide was placed in a catalytic furnace. It was heated at 250-300° and a continuous stream of nitrogen was passed through for 2 hours. The liquid collected in the receiver was extracted with ether. The ether layer was dried with sodium sulfate, the ether distilled off and (III) distilled in vacuum. The b.p. was 134° (at 6 mm). The yield was 9 g (33%). The m.p. was 35-36°.

Found %: C 73.31, 73.12; H 5.62, 5.63. $C_9H_8O_2$. Calculated %: C 72.98; H 5.44.

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* The reaction may be stopped over night.

2-Methyl-5-hydroxybenzofuran was readily soluble in most organic solvents and reacted with an aqueous solution of ferric chloride, giving a cherry red color.

4. Complex of 2-methyl-5-hydroxybenzofuran and p-benzoquinone. 0.5 g of (III) was dissolved in 5 ml of benzine and a saturated solution of 0.36 g of p-benzoquinone in benzene was added. The precipitated red crystals were filtered off, washed with benzine and dried. The yield was 0.5 g. The m.p. was 106-107°.

Found %: C 71.35, 71. 60; H 5.17, 5.17. $C_{24}H_{20}O_6$. Calculated %: C 71.27; H 4.98.

5. 2-Methyl-5-methoxybenzofuran (IV). 7.4 g of (III) was dissolved in 25 ml of 10% sodium hydroxide solution and 6.5 g of dimethyl sulfate added with shaking. The oily layer formed was dried in ether with calcium chloride and distilled in vacuum. The yield of (IV) was 6.3 g. The b.p. was 117-118° (at 10 mm), n_D^{22} 1.5672. According to literature data [1]: b.p. 117-118° (at 10 mm), n_D^{20} 1.5674.

6. 2-Methylbenzofuran-5-hydroxyacetic acid (VI). 1.5 g of (III) and 1.7 g of ethyl bromoacetate was added to an alcohol solution of sodium ethylate prepared from 7 ml of anhydrous alcohol and 0.23 g of sodium. The reaction mixture was boiled for 1 hour on a water bath, then 7 ml of 10% sodium hydroxide solution was added and it was heated for several minutes and diluted with 35 ml of water. The solution formed was filtered. The acid (VI) was isolated by acidifying with hydrochloric acid. The yield was 2 g. The m.p. was 144-145° (from alcohol).

Found %: C 64.15, 64.08; H 5.06, 5.15. $C_{11}H_{10}O_4$. Calculated %: C 64.03; H 4.89.

7. 2-Methyl-5-(p-nitrobenzoxy)-benzofuran (VII). The reaction was carried out under the conditions of experiment 2. For the experiment we used 0.5 g of (III), 0.6 g of p-nitrobenzoyl chloride and 3 ml of pyridine. The yield of (VII) was 0.55 g. The m.p. was 133-134° (from a mixture of alcohol and dioxane 4 : 1).

Found %: C 64.94, 65.05; H 3.89, 3.93. $C_{16}H_{11}O_5N$. Calculated %: C 64.65; H 3.73.

8. Nitroso-2-methyl-5-hydroxybenzofuran (VIII). 1.5 g of zinc chloride and 2 g of (III) was dissolved in 8 ml of anhydrous alcohol. 1 g of sodium nitrite, as a concentrated aqueous solution, was added to the solution. It was heated for 10 minutes on a water bath and kept overnight. The zinc salt was filtered off, washed with alcohol and dissolved in 10% sodium hydroxide solution. The precipitated sodium salt was filtered off and treated with dilute hydrochloric acid. The crystals, which separated, were washed with water. The yield was 2.4 g. The m.p. was 170-171° (from alcohol).

Found %: C 61.32, 61.35; H 4.34, 4.22. $C_9H_7O_3N$. Calculated %: C 61.03; H 3.98.

SUMMARY

Condensation of p-benzoquinone with ethyl acetoacetate gave, in 98% yield, ethyl 2-methyl-5-hydroxybenzofuran-3-carboxylate. From reactions of the latter a series of substituted benzofurans were obtained.

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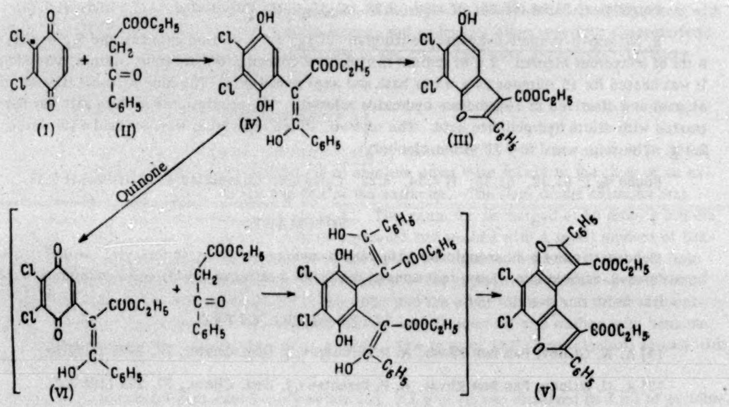
INVESTIGATION IN THE FIELD OF QUINONES

XVII. THE REACTION OF 2,3-DICHLOROQUINONE WITH ETHYL BENZOYLACETATE

A. N. Grinev, N. K. Venevtseva and A. P. Terentyev

As we established [1], 2,3-dichloroquinone reacts with ethyl benzoylacetate. The compound isolated as a result of the reaction was ethyl 6,7-dichloro-2-phenyl-5-hydroxybenzofuran-3-carboxylate. In this work we carried out the condensation of 2,3-dichloroquinone (I) with ethyl benzoylacetate (II) under somewhat different conditions; from this we suceeded in obtaining, besides ethyl 6,7-dichloro-2-phenyl-5-hydroxybenzofuran-3-carboxylate (III), the intermediate hydroquinone (IV) and diethyl 7,8-dichloro-2,5-diphenylbenzo(1,2-b; 5,6-b')-difuran-3,4-dicarboxylate (V). The formation of (IV) and (V) justifies the following scheme for the condensation of 2,3-dichloroquinone with ethyl benzoylacetate:



We were unable to isolate the intermediate quinone (VI). Tars were formed in attempting to obtain it by oxidizing the hydroquinone (IV). Hydroquinone (IV) was converted into a derivative of benzofuran (III) by heating it with zinc chloride in alcoholic solutions under conditions approximately analogous to those of the condensation. In contrast to compounds (III) and (V), hydroquinone (IV) reacted with ferric chloride and p-benzoquinone; the solutions thus formed became dark red, which is explained, apparently, by the formation of compounds of the quinhydrone type.

EXPERIMENTAL

1. Condensation of 2,3-dichloroquinone with ethyl benzoylacetate. 15.5 ml of ethyl benzoylacetate was added to a solution of 8.6 g of zinc chloride in 9 ml of anhydrous alcohol. Then it was heated (85-90°) until it dissolved and 11.1 g of 2,3-dichloroquinone was added portionwise over a period of 20 minutes. After the addition of all the 2,3-dichloroquinone, the mixture was heated for 30 minutes at 85-90°. The reaction mixture was cooled and the crystals separated and washed with 110 ml of ether. The crystals obtained (8.2 g) were dissolved with heating in 168 ml of alcohol. The alcohol solution was cooled and the crystals, which separated, were filtered off and recrystallized from dichloroethane. We obtained 0.8 g of crystals (V) with m.p. 229°, which were soluble in dichloroethane and chloroform and difficultly soluble in alcohol and dioxane.

Found %: C 64.16, 64.02; H 4.03, 3.97. $C_{28}H_{20}O_6Cl_2$. Calculated %: C 64.25; H 3.85.

The alcohol was evaporated off from the alcoholic mother liquor. The crystals formed were recrystallized 3 times from dichloroethane. We obtained 4.1 g of the hydroquinone (IV). The m.p. was 168-170°.

Found %: C 55.22, 55.17; H 3.85, 3.82. $C_{17}H_{14}O_5Cl_2$. Calculated %: C 55.34; H 3.80.

The hydroquinone (IV) was soluble in dichloroethane, alcohol and dioxane; it was difficultly soluble in ether. The compound (IV) gave a dark red color on treatment with ferric chloride and p-benzoquinone in alcohol solutions. After evaporating off the ether from the ethereal mother liquor, we obtained 18.7 g of crystals of the ester (III). The m.p. was 186-187° (from acetic acid). The ester (III) was soluble in ether, alcohol, acetic acid and dichloroethane.

Found %: C 58.34, 58.28; H 3.60, 3,72. $C_{17}H_{12}O_4Cl_2$. Calculated %: C 58.15; H 3.45.

2. Conversion of the intermediate hydroquinone (IV) into ethyl 6,7-dichloro-2-phenyl-5-hydroxybenzofuran-3-carboxylate (III). 1 g of (IV) was dissolved by heating in a mixture prepared from 0.29 g of zinc chloride, 0.5 ml of anhydrous alcohol and 0.5 ml of ethyl benzoylacetate. It was heated for 1 hour at 85-90° and we obtained 0.45 g of (III) with m.p. 186-187° (from alcohol). A mixed melting point with the ester (III), prepared by condensation of 2,3-dichloroquinone with ethyl benzoylacetate, was not depressed.

Found %: C 58.38, 58.47; H 3.63, 3.60. $C_{17}H_{12}O_4Cl_2$. Calculated %: C 58.15; H 3.45.

SUMMARY

It was shown that the condensation of 2,3-dichloroquinone with ethyl benzoylacetate proceeds through the formation of an intermediate hydroquinone and results in a derivative of benzofuran and benzodifuran.

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STEREOCHEMICAL INVESTIGATIONS

II. SYNTHESIS AND DETERMINATION OF THE CONFIGURATIONS OF SOME SUBSTITUTED α-PHENYLETHYLAMINES

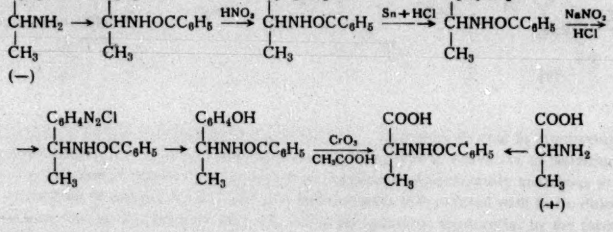
A. P. Terentyev and V. M. Potapov

In a previous report * we briefly mentioned the formation of optically active α-(p-xylyl)-ethylamine (I) and α-(m-xylyl)-ethylamine (II) by resolving the racemates with (-)-menthylsulfuric acid. We prepared the original racemic amines by reductive amination of the appropriate ketones,** by Leikart's method. The reaction was carried out as described in the literature [4], without any complications, and resulted in good yields of the corresponding amines.

It was considerably more difficult to prepare α-(p-nitrophenyl)-ethylamine (III) by a similar method. Of this type of reaction, only the application of the Leikart reaction to m-nitroacetophenone is described in the literature. Ingersoll et al. [5] converted this ketone into amine (III) in a yield of 56% while Nerdel and Liebig [6] did this in 61% yield. Our attempt to apply these methods to the reductive amination of p-nitroacetophenone gave no satisfactory results: much tar was formed and only traces of the required amine (III) could be isolated. We were able to raise the yield of amine (III) to about 50% by lowering the reaction temperature and using formamide or urea with formic acid instead of ammonium formate [7]. (III) could not be resolved into antipodes with (-)-bornylsulfate, however, it was readily resolved with (+)-tartaric acid in an aqueous solution.

To determine the relative configuration of the optically active amines (I), (II) and (III) obtained, we compared the rotation of the amines and their derivatives in different solvents with the rotation of a substance of determined configuration, which was similar to them in structure, namely, α-phenylethylamine (IV).

The relative configuration of α-phenylethylamine was established by Leithe [8] who connected (-)-α-phenylethylamine with (+)-alanine by a series of sucessive reactions, without affecting the asymmetric center.



$$\underset{(-)}{\overset{C_6H_5}{\underset{CH_3}{CHNH_2}}} \rightarrow \overset{C_6H_5}{\underset{CH_3}{CHNHOCC_6H_5}} \xrightarrow{HNO_3} \overset{C_6H_4NO_2}{\underset{CH_3}{CHNHOCC_6H_5}} \xrightarrow{Sn+HCl} \overset{C_6H_4NH_2}{\underset{CH_3}{CHNHOCC_6H_5}} \xrightarrow[HCl]{NaNO_2}$$

$$\rightarrow \overset{C_6H_4N_2Cl}{\underset{CH_3}{CHNHOCC_6H_5}} \rightarrow \overset{C_6H_4OH}{\underset{CH_3}{CHNHOCC_6H_5}} \xrightarrow[CH_3COOH]{CrO_3} \overset{COOH}{\underset{CH_3}{CHNHOCC_6H_5}} \leftarrow \underset{(+)}{\overset{COOH}{\underset{CH_3}{CHNH_2}}}$$

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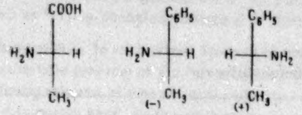
* See Report XXVII in the series "Sulfonation and sulfoacids of acidophobic compounds" [1].

** The ketones could be prepared conveniently by the method described by Mowry et al. [2], which was extended to cover a series of ketones in the work of A. N. Kost, V. P. Ershov and A. P. Terentyev[3].

Apparently, the same distribution of substituents around the asymmetric center is found in the initial (-)-α-phenylethylamine as in (+)-alanine. Consequently, the configuration may be expressed by the following projection formulas.



(+)-alanine α-phenylethylamine

Having established the configuration of α-phenylethylamine by this method, Leithe then [9] carried out the determination of the configuration of a series of related compounds, without relating them directly to chemical conversions, but by comparing the value and direction of their rotations in different solvents with the behavior of α-phenylethylamine under the same conditions. From the analogy of changes in the character of rotation, he concluded that the configurations of the materials being compared were similar. The Leithe method applied here is a development of Freudenberg's work on the determination of relative configuration "by optical comparison"•: the effect of the solvent is considered as "the simplest chemical reaction." An analogous method of determining relative configuration has also been used successfully at the present time (see for example [12]).

In our case, the use of a similar method is facilitated by the fact that the comparison required is of materials extremely close in chemical structure. The determination of the values of specific rotation $[\alpha]_D$ for (I), (II), (III) and (IV) in different solvents gave the results in Table 1.

TABLE 1

Specific Rotation of α-Phenylethylamine and Its Analogs in Different Solvents

Solvent	Amines			
	(I)	(II)	(III)	(IV)**
Without solvent	43.8°	36.1°	13.0°	40.7°
Ether	44.9	37.9	12.3	44.7
Cyclohexane	—	—	—	42.6
Benzene	43.3	39.1	2.3	41.7
Ethylacetate	—	—	—	38.9
Pyridine	—	—	—	38.3
Chloroform	38.9	—	—	35.2
Methyl alcohol	32.7	26.9	12.1	29.0

• Literature data [8].

A comparison of the values given shows that the value of $[\alpha]_D$ in different solvents changes for (I), (II) and (IV), which have the same rotation sign, completely analogously: in ether and benzene it does not differ essentially from the rotation without solvent, in methyl alcohol, however, it decreases noticeably. A comparison of $[\alpha]_D$ for (III) and (IV) shows that their behavior is also generally analogous, although here the parallelism in the changes in $[\alpha]_D$ is less distinctly expressed. Thus, it is possible to conclude, by comparing rotations, that amines with the same rotation sign in this case also have the same relative configuration. However, one cannot consider such a conclusion as completely convincing as the changes in $[\alpha]_D$ in general, are not great (with the

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• The determination of the relative configuration of alanine by comparison with lactic acid may be used as an example of the use of this "optical comparison" [10]. See also the review recently published by Freudenberg [11].

exception of the solution in methyl alcohol) and are not very characteristic. As a check, the amines were converted into the benzoyl derivatives, whose rotations were likewise compared in a series of solvents (Table 2).

TABLE 2

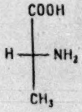
Specific Rotation of Benzoyl Derivatives of α-Phenylethylamine and Its Analogs in Different Solvents

Solvent	Benzoyl derivatives			
	(I)	(II)	(III)	(IV) *
Benzene	74.7°	37.7°	30.5°	39.9°
Ethyl alcohol	— 1.6	—15.0	—15.8	— 0.3
Methyl alcohol	— 2.3	—17.9	—19.4	14.8
Acetone	—28.6	—35.8	—41.0	28.1

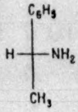
The behavior of the benzoyl derivatives was found to be analogous to that observed for the free amines: the rotation in all cases has a considerable value in benzene and falls greatly in methyl and ethyl alcohols, and even a transition through zero and a change in sign was observed for amines (I), (II) and (III). **

Thus, the behavior of the benzoyl derivatives confirms the original conclusion on the configuration of amine (III) with complete reliability; we prepared this amine by nitrating the optically active amine (IV), using the method described by Baker and Ingold [15] for racemic (IV). The mixture of para and meta isomers thus formed was separated by crystallization of the oxalates. As a result (-)-(IV), which has $[\alpha]_D$ -30° (~75% optical purity) gave (III), which also had a levo rotation ($[\alpha]_D$ −14.2°). At the same time, this experiment showed that the (−)-(IV) obtained by resolving racemic α-phenylethylamine, had an optical purity of the order of 70%.

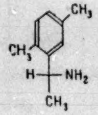
The results given fully corroborate that (+)-(I), (+)-(II) and (+)-(III) have the same relative configuration as (+)-(IV), and as the latter is configuratively related to (-)-alanine, then the relative configuration of all the compounds mentioned should be expressed by the following projection formulas



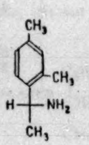
(−)-alanine



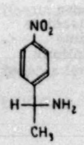
(+)-(IV)



(+)-(I)



(+)-(II)



(+)-(III)

In this way, the relative configuration of compounds (I)-(III) may be considered established but the problem of denoting this configuration remains unsolved. As Freudenberg [16] pointed out in his time, due to its relation to d-(−)-alanine, the amine (+)-(IV) could be defined as "D-(+)-α-phenylethylamine," but by the same ruling it could also be named "L-(+)-α-phenylethylamine" if its configuration is referred to L-phenylaminoacetic acid (V).

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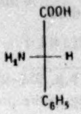
* Literature data [8].

** The chance closeness of $[\alpha]_D$ for benzoyl-α-phenylethylamine in ethyl alcohol to zero, lead Kipping and Hunter [13] to the erroneous conclusion that α-phenylethylamine was racemized by benzoylation. Marckwald and Meth [14] soon pointed out this error.

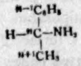
This case is a typical example of possible misunderstandings in denoting configuration, as we have pointed out previously [17]. If in the given cases "ρ - σ-denotation" is used, as proposed in the paper mentioned above, then, taking into account also the precedence of the amino group over hydrogen, (+)-(IV) would be denoted as "(+)- α-phenylethylamine-ρ." Amines (I)-(III) would have analogous denotation.



$$\begin{array}{c} \mathrm{COOH} \\ | \\ \mathrm{H_2N} - \mathrm{C} - \mathrm{H} \\ | \\ \mathrm{C_6H_5} \end{array}$$

(V)

The characteristic property of the "ρ - σ" system is that it is primarily based on a model without being referred to a provisional projection formula. Using Fig. 1, we will briefly explain this system here. In the most general case, an asymmetric atom is part of a carbon chain – open or closed, main or side; two valencies of the atom bond it to the chain, while the third and fourth are occupied by two different substituents, one of which is always "major" (Fig. 1,a) and the other "minor" (Fig. 1, b). Dissimilar sections of the chain are attached to the asymmetric atoms and one of these sections, which includes the start of the enumeration of the chain, will be called "the starting section" (Fig. 1, n-1) and the second –" the end section" (n + 1).



$$\begin{array}{c} {}^{n-1}\mathrm{C_6H_5} \\ | \\ \mathrm{H} - {}^{n}\mathrm{C} - \mathrm{NH_2} \\ | \\ {}^{n+1}\mathrm{CH_3} \end{array}$$

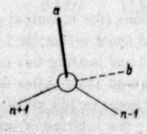


Fig. 1

The configuration of the asymmetric atom would be completely defined, if the relative steric position of the sections of the main chain and of one of the substituents is indicated. For this, let us use the following procedure: let us mentally place the observer on the asymmetric atom in such a way that he would be along the valence bonding the asymmetric atom to the major substituent and would be facing the angle formed by the valencies, to the sections of the main chain. Thus, there are two possibilities, depending on the configuration of the asymmetric atom "n". 1) Atom n-1 (start of enumeration) will be at the left, as in Fig. 1. Such a steric distibution we will provisionally denote by the Greek letter ρ. 2) Atom n-1 (start of enumeration) will be at the right. Such a configuration we will provisionally denote by the Greek letter σ.

The letters ρ and σ were chosen arbitrarily, especially so that they could be related to the following mnemonic rule determining configurations, based on the examination of structure in another projection. This rule is illustrated by Fig. 2. In this figure, n-1 stands out of the paper towards the observer. If the asymmetric atom has a ρ-configuration then, on following the substituents in the basis of the tetrahedron in the order of increasing importance [b < a < (n + 1)], we execute an anti-clockwise movement, similar to the movement in writing the letter ρ. The movement will be reversed for a σ-configuration.

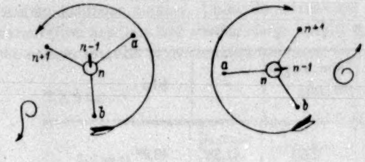


Fig. 2.

If the ρ,σ-configuration is not determined from a steric model but from E. Fischer's projection formulas, we have a ρ-configuration at the given asymmetric atom if on moving along the main chain in the order of the atomic enumeration, the major substituent is on the left of the axis of enumeration.

This system also makes it possible to denote the configuration of compounds with several asymmetric atoms, of cyclic compounds, asimuthal or "atropo-isomers" of the diphenyl type etc. The details are given in the papers mentioned [17].

EXPERIMENTAL

Methyl p-xylyl ketone. To a suspension of 182 g of anhydrous $AlCl_3$ in 360 ml of CCl_4 at 10-15°, stirred mechanically, was added 96 ml of CH_3COCl and then at 15-20° (cooled with running water), 145 ml of p-xylene. After stirring for 2 hours, the reaction mixture was poured into cold water and washed with HCl, water, NaOH solution and again water. The carbon tetrachloride was distilled off (drying was unnecessary as the water distilled off with the first portions of CCl_4) and then the ketone was distilled. We obtained 152.7 g of methyl p-xylyl ketone with b.p. 225-226.5°; the yield was 87%.

α-(p-Xylyl)-ethylamine (I). The methyl p-xylyl ketone prepared (1 mole) was heated with 215 g of ammonium formate by the method [4] and was converted into (I); the yield was 49%.

B. p. 223-225°, n_D^{17} 1.4273, d_4^{17} 0.9439, MR_D 48.60; calc. 48.20.

The benzoyl derivative with m.p. 143° was prepared from (I) by the Schotten-Baumann method.

Found %: C 80.44; H 7.72; N 5.65. $C_{17}H_{19}ON$. Calculated %: C 80.57; H 7.56; N 5.53.

α-(m-Xylyl)-ethylamine (II). We prepared 130.8 g (87%) of methyl m-xylyl ketone with b.p. 228-230° from 1.17 moles of $AlCl_3$ in 450 ml of CCl_4, 82 ml of CH_3COCl and 123 ml of m-xylene similarly to the preceding experiment. From 65 g of the ketone, 154 g of ammonium carbonate and 115 ml of 85% HCOOH, we obtained 30.5 g (47.8%) of α-(m-xylyl)-ethylamine.

B.p 224-227°, n_D^{18} 1.5272, d_4^{18} 0.9487, MR_D 48.32; calc. 48.20. (II) was described previously [18], but the constants were not given.

α-(p-Nitrophenyl)-ethylamine (III). 41 g of p-nitroacetophenone (the technical product, a yellow powder with m.p. 72°), 30 g of urea and 100 ml of 85% HCOOH were heated under reflux for 1 hour (the temperature in the reaction mixture was 117-123°), then the condenser was removed and heating was continued for a further 2 hours in the open flask until a thermometer in the reaction liquid showed 155°. After this it was heated under reflux for 2 hours. The thick black liquid obtained was heated for 2 hours in 100 ml of conc. HCl, filtered hot to remove tars, boiled with charcoal and evaporated down in stages. The mixture of salts obtained was dissolved in water and (III) was separated with concentrated aqueous ammonia. After extracting with ether, drying with potash and distilling in vacuum, we obtained 19.6 g (47.5%) of a yellowish liquid with b.p. 156-160° at 7 mm, which consisted mainly of the amine (III).[•] As the starting technical p-nitroacetophenone contained some of the ortho isomer, the amine (III) contained some α-(o-nitrophenyl)-ethylamine. On standing, the reaction product mainly crystallized and the large prismatic crystals of solid (III) thus formed could be separated from the liquid ortho isomer by suction. Carrying out the reaction with larger amounts of starting material led to a fall in yield. Thus, if we used 1 mole of p-nitroacetophenone, then the yield of (III) was less than 40%.

The benzoyl derivative of (III) had m.p. 151.5° (from benzene). The oxalate had m.p. 206° (from water).

Oxidation of (III) with $KMnO_4$ in an alkaline medium at 95° gave p-nitrobenzoic acid with m.p. 237°; the yield was 96%.

Resolution of α-(p-xylyl)-ethylamine (I). 32.0 g of the barium salt of menthylsulfuric acid $(C_{10}H_{19}OSO_3)_2Ba \cdot H_2O$ (VI) was dissolved in 700 ml of hot water and to the solution was added the equivalent amount of 2 N sulfuric acid by titration. After separating off the precipitate of $BaSO_4$ by centifuging, 15.6 g of amine (I) was added. After cooling, the precipitate was recrystallized 7 times from hot water. We obtained 12.3 g of a salt with m.p. 152-153°, [α]-40.8° (CH_3OH, p 3.7). From decomposition of the latter with 4.2 g of $Ba(OH)_2$ in water, extraction with benzene and distillation, we isolated 4.9 g of the amine (+)-(I), for which the rotation in different solvents was measured (Table 3).

TABLE 3

Solvent	Sample (in g)	Wt. of solution (in g)	Specific gravity of solution	Tube length (in dm)	α	$[\alpha]_D$
Without solvent	—	—	0.944	1.00	41.38°	43.8°
Benzene	0.3623	12.62	0.878	2.00	2.23	43.3
Methyl alcohol	0.2982	11.51	0.798	2.00	1.35	32.7
Acetone	0.3610	11.30	0.799	2.00	2.23	45.2
Dioxane	0.2464	7.13	1.035	1.00	1.42	39.7
Chloroform	0.2700	21.34	1.475	2.00	1.45	38.9
Dibutyl ether	0.4654	11.52	0.771	2.00	2.65	42.4
Diethyl ether	0.3848	9.97	0.723	2.00	2.42	44.9

[•] The vacuum distillation had to be carried out carefully. During the distillation we observed exothermic decomposition of the substance, especially at the end of the distillation.

From (+)-(I) and benzoyl chloride, by the Schotten-Baumann method, we obtained benzoyl-(+)-α-(p-xylyl)-ethylamine with m.p. 110-111° (from CH_3OH), whose rotation values in different solvents are given in Table 4.

TABLE 4

Solvent	Sample (in g)	Wt. of solution (in g)	Specific gravity of solution	Tube length (in dm)	α	$[\alpha]_D$
Benzene.	0.1194	10.72	0.878	2.00	1.46°	74.7°
Methyl alcohol . .	0.1563	11.37	0.80	2.00	—0.05	— 2.3
Acetone.	0.5663	11.85	0.814	2.00	—2.22	—28.6
Ethyl alcohol . .	0.1779	11.55	0.81	2.00	—0.04	— 1.6

Resolution of α-(m-xylyl)-ethylamine (II). Similarly to the preparation of (+)-(I), from 23.52 g of (VI), the equivalent amount of H_2SO_4 and 10.7 g of (II) we obtained a salt, which was recrystallized 7 times to give 4.94 g of a salt, with $[\alpha]^{24}_D$ - 44.3° (CH_3OH, p 3.4) and m.p. 168°, and from which we isolated 1.8 g of (+)-(II). Data on the determination of the optical rotation of (+)-(II) are given in Table 5.

TABLE 5

Solvent	Sample (in g)	Wt. of solution (in g)	Specific gravity of solution	Tube length (in dm)	α	$[\alpha]_D$
Without solvent .	—	—	0.945	0.475	16.21°	36.1°
Ether	0.3090	10.29	0.718	2.00	1.65	37.9
Acetone.	0.2824	11.62	0.795	2.00	1.43	37.0
Benzene.	0.2935	12.73	0.869	2.00	1.57	39.1
Methyl alcohol . .	0.3173	11.29	0.793	2.00	1.20	26.9

From (+)-(II) and C_6H_5COCl we obtained the benzoyl derivative of (+)-(II) with m.p. 131-133° by the Scotten-Baumann method. Under the microscope we clearly observed the conversion of one crystalline modification (fine needles) into another (large prisms) before melting. This conversion occurred at 125.5°. Data on the optical rotation of the benzoyl derivative of (+)-(II) are given in Table 6.

TABLE 6

Solvent	Sample (in g)	Wt. of solution (in g)	Specific gravity of solution	Tube length (in dm)	α	$[\alpha]_D$
Benzene.	0.9227	18.01	0.884	2.00	3.41°	37.7°
Methyl alcohol . .	0.1304	11.31	0.800	2.00	—0.33	—17.9
Acetone.	0.1847	11.51	0.801	2.00	—0.99	—38.5
Ethyl alcohol . .	0.2280	11.68	0.820	2.00	—0.48	—15.0

Resolution of α-(p-nitrophenyl)-ethylamine (III). 63.2 g of (III) and 57 g of (+)-tartaric acid was dissolved in 500 ml of warm water; the precipitate formed was filtered off next morning and twice recrystallized from hot water. We obtained 28.5 g of a salt with m.p. 173-175°, $[\alpha]_D^{20}$ + 12.3°(water, p 2.9).• The salt was dissolved in water and decomposed with conc. NH_3 and the (+)-(III) was extracted with ether and distilled in vacuum. We obtained 17.2 g of (+)-(III);

B. p. 157-159° at 9 mm, d_4^{20} 1.1764, n_D^{20} 1.5688, MR_D 46.26; calc. 45.16.

Data on the rotation of the amine obtained, in different solvents, are given in Table 7.

TABLE 7

Solvent	Sample (in g)	Wt. of solution (in g)	Specific gravity of solution	Tube length (in dm)	α	$[\alpha]_D$
Without solvent	—	—	1.176	1.00	15.32°	13.0°
Benzene	2.7027	12.85	0.930	2.00	0.90	2.3
Methyl alcohol	2.2915	11.50	0.850	2.00	4.09	12.1
Dichloroethane	1.5583	15.26	1.242	2.00	1.95	7.7
Ether	0.7610	9.13	0.742	2.00	1.52	12.3
Dioxane	1.0641	13.09	1.035	2.00	1.75	10.4

From (+)-(III) and oxalic acid (mole to mole) we obtained an oxalate with m.p. 194°.

From (+)-(III) we obtained a benzoyl derivative with m.p. 156-157° (from benzene) by the Schotten-Baumann method.

Found %: C 66.53; H 5.33; N 10.49. $C_{15}H_{14}O_3N_2$. Calculated %: C 66.65, H 5.22; N 10.37.

The rotation of the benzoyl derivative of (+)-(III) in different solvents is given in Table 8.

TABLE 8

Solvent	Sample (in g)	Wt. of solution (in g)	Specific gravity of solution	Tube length (in dm)	α	$[\alpha]_D$
Benzene	0.3670	25.30	0.886	2.00	0.50°	19.5°
Methyl alcohol	0.2994	14.20	0.798	2.00	—0.48	—17.9
Acetone	0.6724	13.77	0.813	2.00	—3.43	—43.2
Dichloroethane	0.3418	19.25	1.249	2.00	—1.60	—36.1
Ethyl alcohol	0.3734	16.92	0.816	2.00	—0.57	—15.8

Nitration of (-)- α-phenylethylamine (IV). 40 ml of HNO_3 (d 1.50) was added over a period of 4 hours with mechanical stirring to 10 g of (-)-(IV) with $[\alpha]_D$ - 30° (optical purity 73.9%) at a temperature from –10 to –4° and after this stirring was continued for a further 1 hour, by which time the temperature had risen to 0°.

• It is difficult to follow the course of the resolution by the $[\alpha]_D$ and the melting point as they hardly change during the recrystallization. However, the crystalline form changes: the salt of the (+)-amine crystallizes as nodules of needles, while when the (-)-amine predominates ball-like growths of a gelatinous character are obtained.

The reaction mixture was poured onto ice, impurities extracted with ether and after making alkaline, the nitroamine was extracted from the aqueous layer with ether. After drying with potash, distilling off the ether and distilling in vacuum, the ether extract yielded 10.2 g of a substance:

B.p. 156-159° at 9 mm, d_4^{20} 1.176, n_D^{20} 1.5645, $[\alpha]_D^{20}$ – 12.8° (without solvent) MR_D 45.96 (calc. 45.40).

To separate the meta and para isomers, the substance obtained was dissolved in 35 ml of water, containing 7.7 g of crystalline oxalic acid. The precipitate formed over several hours was filtered off and recrystallized from water. We obtained 3.8 g of an oxalate with m.p. 195° and by treating this with concentrated aqueous ammonia, extracting with ether and vacuum distilling, we isolated 1.3 g of an amine with b.p. 157-158° at 8 mm, d_4^{20} 1.1741, n_D^{20} 1.5672; $[\alpha]_D$ of the amine obtained, without solvent, was –14.2° and considering that the optical purity of the starting material (IV) was 100%, this gives for optically pure (-)-(III) –19.3°.

Oxidation of 1.0 g of the amine with permanganate in an alkaline medium at the temperature of a boiling water bath yielded 0.89 g of p-nitrobenzoic acid with m.p. 236°.

SUMMARY

1. Reductive amination of methyl p-xylyl ketone, methyl m-xylyl ketone and p-nitroacetophenone by Leikart's method gave α-(p-xylyl)-ethylamine (I), α-(m-xylyl)-ethylamine (II) and α-(p-nitrophenyl)-ethylamine (III), respectively, which were resolved into optical antipodes with the isolation of the (+)-forms.

2. We determined the relative configuration of the optically active amines obtained.

3. (-)-α-Phenylethylamine was converted directly into (-)-α-(p-nitrophenyl)-ethylamine by nitration which confirmed the conclusions on its relative configuration, arrived at by comparing the rotation of the amine and its benzoyl derivative in different solvents with the behavior of α-phenylethylamine.

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INVESTIGATION OF PULEGONE OXIDE

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In a report devoted to the investigation of pulegone oxide, N. A. Prilezhaev [1] described the peculiar properties of the oxide which he synthesized: when it is heated it readily changes into a liquid modification of the same structure. Intrigued by this phenomenon, we set ourselves the problem of finding out the reason for the change in the physical state of pulegone oxide, that occurs as a result of its being heated. We prepared pulegone oxide from pulegone. It possessed all the properties noted by N. A. Prilezhaev, except for optical activity. Contrary to the data of the above investigator, the oxide rotated the plane of polarization (α_D + 10.28°). Its coefficient of rotational dispersion, as for pulegone, is high ($\frac{\alpha_v}{\alpha_j}$ 1.23). It should be noted that pulegone oxide is partially enolized by Grignard reagents.

To elucidate the conditions for obtaining the liquid modification, we heated pulegone oxide systematically, for a long time at 200°. At the same time we determined the rotation of the plane of polarization, as we considered that it could reflect fine differences in changes of structure, accompanying the transition from the crystalline into the liquid modification. The data obtained in these experiments (table) show that as the pulegone oxide was heated its rotatory power increased, reaching a significant value (+35.08°) after 10 hours; at the same time the coefficient of rotational dispersion changed little. No increase in the degree of enolization was observed. The combination scattering spectrum of pulegone oxide did not change when the latter was heated to 200°. The only difference in the spectra of the crystalline and liquid modification worth mentioning lies in the intensity of separate spectral lines.

There are definitely no deep structural changes which occur in the pulegone oxide molecule during heating. In this connection our results confirm N. A. Prilezhaev's conclusions.

Change in the Rotatory Power of Pulegone Oxide as a Result of Heating at 200° in a Current of Nitrogen

	Before heating	After heating for:		
		5 hours*	8 hours**	10 hours**
α_D	+10.28°	+18.44°	+28.84°	+35.08°
α_j	+11.08	+20.08	+30.64	+44.09
α_v	+13.61	+23.24	+35.60	+50.45
$\frac{\alpha_v}{\alpha_j}$	1.23	1.15	1.16	1.15

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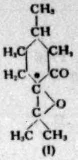
* The material partially recrystallized after 15 days.

** The material did not recrystallize. After heating, the oxide was distilled in vacuum.

We consider that the change in the physical state of pulegone oxide is related to its rotatory power. If we turn our attention to the structure of pulegone and the oxide, prepared from it, we see that a new asymmetric atom, denoted by a star in formula (I), is produced during the formation of the oxide. Due to the presence of an existing optically active asymmetric atom the new asymmetric atom will be optically active [2]. A considerable decrease in the rotatory power of pulegone oxide (α_D + 10°) in comparison with that of the initial pulegone (α_D + 20.6°) can be explained, apparently, by the new asymmetric center causing a levo rotation. When the pulegone oxide is heated, however, one of the diastereomers is converted into another, according to the scheme: + A – B ⟶ + A + B. This explains both the change in the rotation of the plane of polarization and the changes in the physical properties of pulegone oxide. The similarity in combination scattering spectra also becomes clear. Diastereometry may also affect the intensity of the spectral lines, leaving unchanged the $\Delta\nu$ frequencies which characterize particular atomic oscillations in molecules which differ only in steric structure.


(I)

EXPERIMENTAL

Preparation of pulegone oxide. The pulegone used for the synthesis of the oxide was isolated from pennyroyal oil.

B. p. 107-108° (17 mm), d_4^{20} 0.9339, n_D^{20} 20 1.4821, $[\alpha]_D$ + 20.04°.

The pulegone oxide was prepared by Prilezhaev's method, by oxidizing pulegone with benzoyl peroxide. It had the following constants:

m. p. 43-45°, b. p. 137-138° (24 mm), α_D + 10.28°.

The number of hydroxyls before heating the oxide was 0.24. The number of hydroxyls after heating the hydroxide for 8 hours was 0.20.

Combination light scattering spectra. The spectra were plotted with an ISP-51 spectrograph using the blue line (λ = 4358 A°) of the mercury spectrum.

The crystalline modification of pulegone oxide (in the fused state). The exposure time was 6 hours; the slit 0.005 mm; the light filter – ZhS-2 glass. $\Delta\nu$ (in cm^{-1}):

337 (1), 369 (1), 394 (3 broad), 491 (3), 606-627-636 (5; band), 724 (3), 776 (2 broad), 819 (1), 835 (2 broad), 874 (1), 1074 (2 broad), 1183 (3 broad), 1239 (2), 1275 (3), 1328 (2 broad), 1390 (3 broad), 1456 (5), 1719 (8), 2870 (3 broad), 2924 (3 broad), 2970 (3 broad).

The liquid modification of pulegone oxide (after 8 hours heating at 200°). The exposure time was 9 hours; the slit 0.008 mm; due to slight coloring of the substance, the spectrum was plotted without the light filter. $\Delta\nu$ (in cm^{-1}):

336 (1), 364 (3), 392 (3), 603-621-634 (5; band), 719 (2), 775 (2 broad), 816 (3), 843 (3), 878 (0), 1097 (5 broad), 1157 (5 broad), 1196 (6 broad), 1230 (0), 1274 (1), 1328 (2), 1388 (3), 1452 (3), 1653 (0), 1717 (8), 2870 (5), 2924 (5), 2969 (5 broad).*

SUMMARY

Pulegone oxide has a rotatory power α_D + 10.28°. The transition of pulegone oxide, when heated, into a liquid modification is accompanied by an increase in rotatory power up to α_D + 35.08°.

We explain the formation of the liquid modification of pulegone oxide as a transition of one diastereomer into another.

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* The lines with frequencies $\Delta\nu$ 1097 (5 broad), 1157 (5 broad) and 1196 (6 broad) cm^{-1} were "false," excited by the mercury line λ4046 A°. The weak line with the frequency $\Delta\nu$ 1653 cm^{-1} may correspond to the enol form of pulegone oxide.

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MERCAPTO ANALOGS OF LYSINE AND SOME OF ITS DERIVATIVES

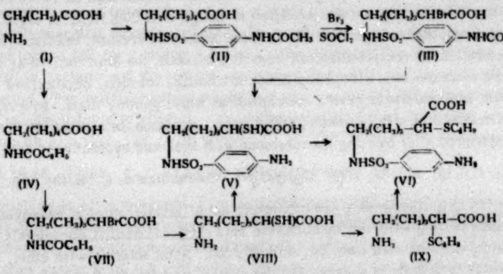
II. SYNTHESIS OF α-MERCAPTO-ε-AMINO- AND α,ε-DIMERCAPTOCAPROIC ACIDS AND THEIR S-ALKYL AND N-SULFANYLYL DERIVATIVES

Yuan Chen-e and M. N. Shchukina

α-Mercapto-ε-aminocaproic acid was synthesized in 1935 as its hydrochloride by treating α-bromo-ε-benzoylaminocaproic acid with potassium xanthate with subsequent hydrolysis [1]. The preparation of its derivatives substituted at the mercapto- and amino-groups is not described in the literature.

There is no information on α,ε-dimercaptocaproic acid in the literature.

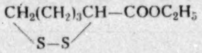
We prepared α-mercapto-ε-aminocaproic acid (VIII) by treating α-bromo-ε-benzoylaminocaproic acid (VII) with potassium hydrosulfide with subsequent hydrolysis of the benzoyl group with hydrochloric acid. The mercaptoamino acid thus synthesized contained many impurities and was purified through the lead salt and obtained in a crystalline form. The presence of free mercapto- and amino-groups in the compound synthesized by us, was proved by the formation of S-alkyl and N-sulfanyl derivatives. The reactions carried out are shown in the scheme


CH₂(CH₂)₄COOH NH₂
(I)
CH₂(CH₂)₄COOH NHSO₂–C₆H₄–NHCOCH₃
(II)
Br₂ SOCl₂
CH₂(CH₂)₃CHBrCOOH NHSO₂–C₆H₄–NHCOCH₃
(III)
CH₂(CH₂)₄COOH NHCOC₆H₅
(IV)
CH₂(CH₂)₃CH(SH)COOH NHSO₂–C₆H₄–NH₂
(V)
CH₂(CH₂)₃–CH(COOH)–SC₄H₉ NHSO₂–C₆H₄–NH₂
(VI)
CH₂(CH₂)₃CHBrCOOH NHCOC₆H₅
(VII)
CH₂(CH₂)₃CH(SH)COOH NH₂
(VIII)
CH₂(CH₂)₃CH–COOH NH₂ SC₄H₉
(IX)

Starting with the α-mercapto-ε-aminocaproic acid (VIII) obtained, we prepared α-S-butylmercapto-ε-aminocarboxylic acid (IX) by alkylation using Seebeck's method [2] in an aqueous alkaline medium and α-mercapto-ε-(p-aminobenzenesulfonamido)-carboxylic acid (V) – by condensation with p-acetylaminobenzenesulfonyl chloride and subsequent hydrolysis of the condensation product. Both the acids mentioned above were converted into the same α-S-butylmercapto-α-(p-aminobenzenesulfonamido)-caproic acid (VI) by a series of reactions.

Condensation of p-acetylaminobenzenesulfonyl chloride with ε-aminocaproic acid (I) by the Schotten-Baumann method gave ε-(p-acetylaminobenzenesulfonamido)-caproic acid (II). Bromination of this acid in a chloroform medium in the presence of thionyl chloride gave α-bromo-ε-(p-acetylaminobenzenesulfonamido)-caproic acid (III) which was then converted into α-mercapto-ε-(p-aminobenzenesulfonamido)-caproic acid (V) by treating with excess potassium hydrosulfide and subsequent hydrolysis. We found that acid (V) was identical with the compound obtained by treating α-mercapto-ϵ-aminocaproic acid (VIII) with p-acetylaminobenzenesulfonyl chloride and subsequent hydrolysis. It should be noted that the attempt to brominate ϵ-(p-acetylaminobenzenesulfonamido)-caproic acid (II) in the presence of red phosphorus by the method used for the synthesis of α-bromo-ϵ-benzenearninocaproic acid, ended in failure as the material was completely resinified.

Ethyl α,ϵ-dimercaptocaproate was prepared by treating ethyl α,ϵ-dibromocaproate with potassium hydrosulfide in an alcoholic medium with prolonged heating; it was found that the substitution of two halogens for the mercapto groups proceeded with much more difficulty than in the case of mono-substituted acids. Ethyl 1,2-dithiocycloheptan-3-carboxylate – the inner disulfide ester of α,ϵ-dimercaptocaproic acid – was isolated as a side product by distilling the ester obtained. The formation of inner cyclic disulfides from dimercapto substituted derivatives has been described for other similar compounds [3]. Ethyl α,ϵ-dimercaptocaproate gives all reactions, characteristic of mercapto compounds. When alkylated under the usual conditions, it forms ethyl α-, ϵ-di-S-ethylmercaptocaproate in good yield.



In investigating some preparations obtained in the division of chemotherapy of cancer of the All-Soviet Chemico-Pharmaceutical Research Institute, V. A. Chernov found that α-mercapto-ϵ-aminocaproic acid had clearly expressed anti-tumor activity in an experiment on animals in vitro as well as in vivo.

EXPERIMENTAL

1. α-Mercapto-ϵ-benzoylaminocaproic acid. 3.14 g of α-bromo-ϵ-benzoylaminocaproic acid (VII) [4] was added to a suspension of 1.5 g of KSH in 50 ml of alcohol and the mixture was heated on a boiling water bath for 1 hour. After cooling, the precipitate was filtered off and washed with alcohol. The alcohol solution was evaporated to dryness in vacuum and the oily residue obtained was dissolved in 10 ml of 10% soda. After treating with charcoal, the alkaline solution was acidified to Congo with 20% HCl. A crystalline precipitate was formed. The substance was difficultly soluble in benzene and ethyl acetate, readily soluble in 50% alcohol and more soluble in acetone. After recrystallization from 50% alcohol, the acid melted at 152-157° (literature data [1]: m.p. 158°), gave a voilet color with nitroprusside in alkaline solution, decolorized a 0.1 N solution of iodine in alcohol and with lead acetate it gave a mercaptide as white gummy mass. By evaporating the alcoholic mother liquor, we obtained an oily substance, which gave a reaction for a disulfide bond. The reaction for a free sulfhydryl group appeared after treating the substance with zinc and hydrochloric acid.

Found %: C 58.24; H 6.48; N 5.22, 5.20. $C_{13}H_{17}O_3NS$. Calculated %: C 58.43; H 6.36; N 5.24.

2. The hydrochloride of α-mercapto-ϵ-aminocaproic acid. α-Mercapto-ϵ-benzoylaminocaproic acid (IV) (5 g) was hydrolyzed by boiling with 20% hydrochloric acid (100 ml) until it completely dissolved (18 hours). After cooling, benzoic acid was separated from the acid solution. After washing with ether, the hydrochloric acid solution was evaporated to dryness in vacuum and the residue was dissolved in 50 ml of water and treated with 40 ml of 10% lead acetate solution with vigorous shaking. The crystalline lead mercaptide formed was washed with water, dissolved in 60 ml of warm 10% hydrochloric acid and treated with hydrogen sulfide. The precipitate of lead sulfide was filtered off and the solution evaporated to dryness in vacuum. Several portions of water were added to the oily substance obtained and evaporated off (to remove excess hydrogen chloride) and then benzene. The residue was dried in vacuum over P_2O_5 and NaOH and kept for 8 days at –10°. The substance which crystallized out was dissolved in 15 ml of boiling anhydrous alcohol and the solution was treated with charcoal. After adding dry ether (10 ml), the hydrochloride of α-mercapto-ϵ-aminocaproic acid crystallized out in the form of prisms on cooling. The m.p. was 122-124.5° (with decomp.). Literature data [1]: m.p. 117-123°. The substance gave characteristic reactions for a mercapto group. The yield was 1.55 g (41.5%).

3. Ethyl α-mercapto-ϵ-aminocaproate. A solution of 4 g of the hydrochloride of α-mercapto-ϵ-aminocaproic acid in 80 ml of anhydrous alcohol was saturated with dry hydrogen chloride in the cold. After 2 days the alcohol solution was evaporated to dryness in vacuum and the oily residue was treated with sodium bicarbonate solution (40 ml). The oil which separated was extracted with ether (40 ml). The ether extract was dried

with sodium sulfate and evaporated in a stream of nitrogen to give 3 g of a dark, oily substance, which was then twice distilled at 2 mm (b.p. 182-184°). Ethyl α-mercapto-ε-aminocaproate was a colorless, mobile, oily substance, which gave reactions for a free mercapto group (with iodine and lead acetate solutions) and was readily soluble in alcohol and ether, moderately soluble in sodium hydroxide solution (from which a precipitate came down on standing – disulfide) and insoluble in a saturated solution of sodium bicarbonate.

Found %: C 50.39; H 9.02; N 7.48. $C_8H_{17}O_2NS$. Calculated %: C 50.02; H 8.90; N 7.32.

4. The hydrochloride of α-butylmercapto-ε-aminocaproic acid. 6.7 g of butyl iodide was added to a solution of 3.6 g of unpurified α-mercapto-ε-aminocaproic acid hydrochloride, 20 ml of alcohol and 21 ml of 2 N NaOH at a temperature no higher than 25°. The reaction mixture was stirred in a stream of nitrogen at room temperature for 15 hours, after which it was acidified to Congo with 20% HCl. The unreacted butyl iodide was separated off and the solution washed with ether. The hydrochloric acid solution was evaporated to dryness in vacuum and the residue obtained was dissolved in 50 ml of water and treated with charcoal. The aqueous solution was again evaporated in vacuum and the residue extracted with boiling, anhydrous alcohol. After distilling off the alcohol in vacuum, we obtained a dark sirupy residue, which crystallized on being cooled strongly and rubbed with petroleum ether. The substance obtained was washed with a small amount of cold 10% hydrochloric acid. The yellowish powder, with m.p. 223-226°, did not give a characteristic reaction for a free mercapto group with a solution of iodine or lead acetate. The yield was 3.78 g (82.3%). For purification the substance was dissolved in 6 ml of anhydrous alcohol by heating and the solution treated with charcoal. 5 drops of conc. HCl was added to the clear filtrate. On cooling strongly, a colorless crystalline substance with m.p. 228-230° precipitated from the turbid solution. The hydrochloride of α-butylmercapto-ε-aminocaproic acid was soluble in water and alcohol; it was difficultly soluble in cold hydrochloric acid and practically insoluble in the usual organic solvents.

Found %: N 5.46, 5.41; Cl 14.00. $C_{10}H_{21}O_2NS \cdot HCl$. Calculated %: N 5.48; Cl 13.89.

5. α-Bromo-ε-(p-acetylaminobenzenesulfonamido)-caproic acid (III). A mixture of 5 g of dry ε-(p-acetylaminobenzenesulfonamido)-caproic acid (II), 20 ml of freshly distilled thionyl chloride and 10 ml of dry chloroform was heated with stirring at 60° for 30 minutes. The substance dissolved and formed a dark brown solution. After cooling to room temperature, 5.3 g of dried bromine and 5 ml of dry chloroform were added to the solution. Then the reaction mixture was gradually heated to 50° on a water bath and kept at this temperature for 2 hours and then at 90° for a further 1.5 hours. The following day, the solvent and excess thionyl chloride was distilled off in vacuum and the residue was poured into water and ice (125 ml). The precipitated oil crystallized on stirring. The reddish-yellow precipitate was filtered off and washed with water. The substance obtained was very readily soluble in alcohol. On adding water (1 : 15) to its alcohol solution, a light yellow precipitate formed with m.p. 125-128° (with decomp.).

Found %: Br 19.56, 19.89. $C_{14}H_{19}O_5N_2SBr$. Calculated %: Br 19.66.

6. The hydrochloride of α-mercapto-ε-(p-aminobenzenesulfonamido)-caproic acid. a) From the hydrochloride of α-mercapto-ε-aminocaproic acid. The experiment was carried out similarly to that which we described for the synthesis of N-(p-aminobenzenesulfonyl)-D,L-cysteine [5]. From 1.2 g of the hydrochloride of α-mercapto-ε-aminocaproic acid, 0.2 g of sodium hydrosulfite and 1.4 g of p-acetylaminobenzenesulfonyl chloride we obtained 0.8 g (37.8%) of the hydrochloride of α-mercapto-ε-(p-aminobenzenesulfonamido)-caproic acid. The m.p. was 182-187° (with decomp.); the colorless crystals were readily soluble in alcohol, water and alkalis and difficultly soluble in cold hydrochloric acid. The alcohol solution gave a crystalline precipitate with lead acetate.

Found %: N 7.95, 7.96; Cl 10.13, 10.23. $C_{12}H_{18}O_4S_2N_2 \cdot HCl$. Calculated %: N 7.91; Cl 10.01.

b) From α-bromo-ε-(p-acetylaminobenzenesulfonamido)-caproic acid (III). 4.07 g of α-bromo-ε-(p-acetylaminobenzenesulfonamido)-caproic acid was added to a suspension of 1.5 g of KSH in 50 ml of alcohol. The mixture was heated on a boiling water bath for 1.5 hours. The precipitate of potassium bromide was filtered off and the alcohol solution evaporated to dryness in vacuum. The oily substance obtained was hydrolyzed by boiling with 20 ml of 15% hydrochloric acid until it completely dissolved (1 hour). After treating with charcoal, the hydrochloric acid solution was evaporated down to half its volume in vacuum. On cooling, a yellowish crystalline substance precipitated, which, after 2 recrystallizations from 10% hydrochloric acid, had m.p. 182-187°

(decomp.) and did not depress the melting point of the hydrochloride of α-mercapto-ε-(p-aminobenzenesulfonamido)-caproic acid, synthesized by the method described above. The yield was 1.8 g (50.5%).

7. The hydrochloride of α-butylmercapto-ε-(p-aminobenzenesulfonamido)-caproic acid. a) A solution of 1.8 g of the hydrochloride of α-S-butylmercapto-ε-aminocaproic acid in 30 ml of 1 N sodium hydroxide was treated with p-acetylaminobenzenesulfonyl chloride (1.98 g), as described for the preparation of the hydrochloride of α-(p-aminobenzenesulfonamido)-ε-S-butylmercaptocaproic acid [6]. After hydrolysis, a crystalline substance was isolated from the acid solution. Recrystallization from 10% hydrochloric acid gave a colorless crystalline substance with m.p. 171.5-172.5°, which was readily soluble in water and with difficulty in cold, dilute hydrochloric acid. The yield was 2.26 g (78.5%).

Found %: N 6.84; Cl 8.64; 8.93. $C_{16}H_{26}O_4N_2S_2 \cdot HCl$. Calculated %: N 6.82; Cl 8.64.

b) A mixture of 0.6 g of the hydrochloride of α-mercapto-ε-(p-aminobenzenesulfanilamido)-caproic acid, 0.65 g of butyl iodide in 6 ml of alcohol and 7 ml of 1 N NaOH was shaken in a closed vessel, filled with nitrogen, for 20 hours at room temperature. After this the alkaline solution was heated on a water bath with stirring for 20 minutes and then 8 ml of water was added to it. On cooling, the aqueous solution was filtered and washed with ether. By acidifying the aqueous solution to Congo with conc. HCl we obtained a yellowish precipitate, which was twice recrystallized from 10% HCl. The substance obtained melted at 170-172° and did not depress the melting point of the hydrochloride described above. The yield was 0.32 g (46.2%).

8. Ethyl α, ε-dimercaptocaproate. A solution of 16 g of ethyl α,ε-dibromocaproate in 20 ml of alcohol was added to a suspension of 15.3 g of KSH in 150 ml of alcohol. The mixture was heated on a boiling water bath for 18 hours. The reaction mixture was then treated as described for the preparation of the ester of α-mercaptocaproic acid [6]. By evaporation of the dry ether extract, we obtained 8.91 g of an oily substance, which gave a negative reaction for halogen and a positive one for sulfur. The substance obtained was fractionally distilled in vacuum: 1st fraction, b.p. 100-102° (1.1 mm), 2.75 g (25%); 2nd fraction, b.p. 187.5-189° (0.9 mm), 4.60 g (41.7%).

The 1st fraction formed a yellow crystalline mercaptide with lead acetate and decolorized a solution of iodine in alcohol. It was ethyl α,ε-dimercaptocaproate.

d_4^{20} 0.9865, n_D^{20} 1.4452, MR_D 56.138; calc. 56.178.

Found %: C 46.16, 46.39; H 7.70. 7.88; S 30.50. $C_8H_{16}O_2S_2$. Calculated %: C 46.15; H 7.69, S 30.77.

The 2nd fraction gave a reaction for a free sulfhydryl group only after treatment with zinc and hydrochloric acid. The substance was the cyclic inner disulfide – ethyl 1,2-dithiocylcoheptanecarboxylate-3.

Found %: C 46.26; H 6.75; S 30.78. M 198.8. $C_8H_{14}O_2S_2$. Calculated %: C 46.40; H 6.80; S 31.07. M 206.3.

9. Ethyl α,ε-diethylmercaptocaproate. A solution of 2.08 g of ethyl α,ε dimercaptocaproate in 5 ml of alcohol was added to a solution of alcoholate, prepared from 0.46 g of sodium in 30 ml of anhydrous alcohol, followed by 6.24 g of ethyl iodide. The mixture was heated on a water bath at 60-70° for 12 hours and at the boiling point of the solvent for a further 8 hours, after which the reaction medium remained neutral to litmus. The contents of the flask were treated as described for the preparation of the ester of ε-ethylmercapto-n-caproic acid [6]. The residue obtained by evaporating down the ether extract was distilled at 0.8 mm and a fraction was collected with b.p. 134-136°. The yield was 2.15 g (81.15%).

d_4^{20} 0.9989, n_D^{20} 1.4753, MR_D 74.221; calc. 73.410.

Found %: C 54.79, 54.69, H 9.10, 9.32. $C_{12}H_{24}O_2S_2$. Calculated %: C 54.55; H 9.09.

SUMMARY

1. α-Mercapto-ε-amino- and α,ε-dimercaptocaproic acids as well as their S-butyl- and N-sulfanyl derivatives were synthesized.

2. It was established that ethyl 1,2-dithiocycloheptan-3-carboxylate – an inner cyclic disulfide – was formed by the α- and ε-mercapto groups when ethyl α,ε-dimercaptocaproate was distilled.

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THE PROBLEM OF THE GENERAL DEFINITION OF CHEMISTRY

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There is no need to prove the necessity for reexamination and more accurate specification of antiquated definitions, names and terms in a science as it develops; therefore, Yu. A. Zhdanov [1] is quite correct in considering that it is necessary to define chemistry more accurately. But for this it is necessary to prove adequately the disadvantages of the existing definition and the advantages of the new one.

Zhdanov considers that the definition of chemistry as the science of materials and their conversions is very inaccurate. The reasoning is that such phenomena as changes in the state of aggregation of bodies, many of the polymorphous conversions and radioactive decay, are connected with conversion of material, but nevertheless, are not strictly within the scope of chemistry. These conclusions cannot be considered convincing. After all, neither changes in the state of aggregation of bodies nor polymorphous conversions are connected with conversions of material, and therefore they should not fall "strictly within the scope of chemistry." In connection with radioactive decay, there is, actually, conversion of material. It is true that these conversions occur as a result of changes, not in the outer electronic shell of the atom, as in the case of normal chemical reactions, but in the atomic nucleus. Nuclear reactions occur which are the subjects of investigation in both physics and chemistry. Consequently, Zhdanov's objection to the definition of chemistry as the science of materials and their conversions is not adequately substantiated.

Engels, investigating the law of the transition of quantity into quality and the reverse, stresses the effect of this law on phenomena, studied in the natural sciences. But this law has its greatest effect in the chemical field. Therefore, "chemistry," as Engels said, "may be called the science of qualitative changes in bodies, occurring as a result of changes in the quantitative composition" [2]. Zhdanov considers this idea of Engels as a definition of chemistry and remarks that Engels' definition does not cover numerous cases of the isomerism of organic and inorganic compounds. It seems to us that Engels' statement cannot be considered a general definition of chemistry, that is, an all inclusive definition which would conver all chemical phenomena and, in particular, the phenomenon of isomerism, the nature of which was quite well known to Engels.

In connection with the law of the transition of quantity into quality, we should note that this law is manifested in the isomerism of chemical compounds and not just in that the quantity of atoms in a molecule, starting from a definite value, controls the possibility and actual existence of qualitatively different isomers. This law also finds expression in isomeric compounds in the fact that qualitative changes in the isomeric material are due to definite quantitative changes occurring in it. The main difference in isomeric compounds lies in the chemical molecular structure which is a qualitative definitive, owing its existence to the fact that each atom, entering the composition of a molecule, acts with a definite amount of the chemical power belonging to it. A mutual bond and effect exists between these atoms.

In agreement with present day ideas which develop from Butlerov's theory, the chemical structure of a molecule is controlled by the valence state of the atoms forming the molecule, their steric disposition, the character of the distribution of electronic density, interatomic distances etc. All these factors are of a quantitative character; they determine the chemical structure of a molecule and its physical and chemical properties, by which the quality of the material is expressed. In isomeric phenomena a series of these quantitative factors are changed, as a result of which qualitative changes in the isomeric compounds take place. Therefore, it is incomprehensible why Zhdanov considers that it is difficult to refer the differences in properties, for example of isomeric methylchrysenes, to the transition of quantitative changes into qualitative ones [1].

After all, the distribution of electronic density and interatomic distances change in these compounds with changes in the position of the methyl group. The bond energy between the methyl group and the aromatic nuclei also changes. Is this not a quantitative change causing changes in the properties of isomeric methylchrysenes?

Zhdanov, apparently wishing to affirm the possibility of qualitative changes without quantitative changes, gives Engels' statement: "... but one should also examine the numerous qualitative changes, whose dependence on quantitative changes is not at all established. One may readily agree that the current tendency in science is in this direction, but this does not prove that it is the only correct one and that by following this tendency, we will completely exhaust physics and chemistry" [2]. This does not mean that Engels recognizes the possibility of qualitative changes without quantitative ones. This would contradict Engels' categorical statement: "It is impossible to change the quality of any body without the addition or removal of matter or motion, i.e. without quantitative change" [2]. If one reads to the end of the article "The Mechanical Comprehension of Nature" which includes the statement by Engels that is quoted by Zhdanov, it becomes clear that Engels does not eliminate the dependence of qualitative changes on quantitative ones. Engels here is against "the mechanical" conception, which exclusively reduces all qualitative differences to quantitative ones "without noting that the relation between quality and quantity is mutual, that quality also changes into quantity, as quantity changes into quality and that there is interaction here"[2].

In concluding his article, Zhdanov proposed the following definition of chemistry "Chemistry is the science of qualitative changes in bodies, caused by the effect of changes in their quantitative composition and structure" [1].

The definition given has the following disadvantages:

1. At present "body" is usually understood to mean a geometrical or physical body; and therefore it is not obvious that Zhdanov is speaking of changes in material.

2. This definition talks of qualitative changes caused by the effect of changes in quantitative composition and structure. One should assume that if some phenomenon does not satisfy even one of the requirements of this definition it cannot be studied in chemistry. In this case, what can be done with the phenomenon of isomerism where the quantitative composition does not change and only the structure changes?

3. The chemical structure of a material is an intrinsic quality which determines its chemical behavior and therefore Zhdanov's formulation "Qualitative changes in bodies caused by the changes ... in structure" is to some extent, tautological.

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